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(54) DIELECTRIC PORCELAIN COMPOSITION, ELECTRONIC PART AND METHOD FOR PRODUCING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a dielectric porcelain composition which can be sintered at a temperature of $\leq 1,200^{\circ}$ C in a non-oxidizing atmosphere but has a high dielectric constant, to provide a method for producing the same, and to provide an electronic part, such as a chip capacitor, which can be sintered at low temperature and whose insulating resistance accelerated life is improved.

SOLUTION: This dielectric porcelain composition comprises a main component containing a dielectric oxide having a composition represented by $\{[Ba(1-x)Ca_x]O\}A(Ti(1-y)Zry)BO_2$ and a subsidiary component containing one or more substances selected from the oxides of Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Dd, Ti, Sn, W, Mn, Si and P and/or compounds giving the oxides after sintered. The subsidiary component is contained in an amount of 0.001 to 5% in terms of the oxides on the basis of the total amount of the composition. The symbols A, B, (x), and (y) exhibiting the composition ratio in the formula representing the main component have the relations: $0.990 \leq A/B < 1.000$, $0.01 \leq (x) \leq 0.25$, and $0.1 \leq (y) \leq 0.3$.

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(54)【発明の名称】 誘電体磁器組成物、電子部品およびそれらの製造方法

(57)【要約】

【課題】 非酸化性雰囲気で1200℃以下の温度での
焼成が可能であるにもかかわらず、高い誘電率を有する
誘電体磁器組成物およびその製造方法を提供すること
と、低温焼成が可能で、しかも絶縁抵抗の加速寿命が向
上されたチップコンデンサなどの電子部品を提供すること。

【解決手段】 $\left\{ \left(\begin{array}{c} \text{B a}_{(1-x)} \text{C a}_x \end{array} \right) \text{O} \right\}$
 $\times \left(\begin{array}{c} \text{T i}_{(1-y)} \text{Z r}_y \end{array} \right) \text{B}_2\text{O}_3 \text{O}_2$ で示される組
成の誘電体酸化物を含む主成分と、Sr, Y, Gd, T
b, Dy, V, Mo, Zn, Cd, Ti, Sn, W, M
n, Si およびPの酸化物および/または焼成後にこれ
らの酸化物になる化合物から選ばれる1種類以上を含む
副成分とを有し、前記副成分が、組成物全体に対して、
酸化物換算で、0.001~5%含まれ、前記主成分を
示す式中の組成比を示す記号A, B, x, yが、0.9
 $9.0 \leq A/B < 1.000$ 、 $0.01 \leq x \leq 0.25$ 、
 $0.1 \leq y \leq 0.3$ の関係にあることを特徴とする誘電
体磁器組成物。

【特許請求の範囲】

【請求項1】 $\left\{ \left(\text{Ba}_{(1-x)} \text{Ca}_x \right) \text{O} \right\} \wedge \left(\text{Ti}_{(1-y)} \text{Zr}_y \right)_B \text{O}_2$ で示される組成の誘電体酸化物を含む主成分と、

$\text{Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si}$ および P の酸化物および/または焼成後にこれらの酸化物になる化合物から選ばれる1種類以上を含む副成分とを有し、

前記副成分が、組成物全体に対して、酸化物換算で、

$0.001 \sim 5$ モル%含まれ、

前記主成分を示す式中の組成比を示す記号 A, B, x, y が、

$0.990 \leq A/B < 1.000$ 、

$0.01 \leq x \leq 0.25$ 、

$0.1 \leq y \leq 0.3$ の関係にある誘電体磁器組成物。

【請求項2】 組成物全体に対して、 Li の酸化化合物および/または焼成後に Li の酸化化合物となる化合物を、酸化物 (Li_2O) 換算で $0.01 \sim 1.5$ モル%含有することを特徴とする請求項1記載の誘電体磁器組成物。

【請求項3】 焼成後の誘電体磁器組成物が、 Li の酸化化合物および/または焼成後に Li の酸化化合物となる化合物を、酸化物 (Li_2O) 換算で $0.01 \sim 1.0000 \text{ ppm}$ 含有することを特徴とする請求項1または請求項2記載の誘電体磁器組成物。

【請求項4】 $\text{Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si}$ および P の酸化物および/または焼成後にこれらの酸化物になる化合物から選ばれる1種類以上を含む副成分を含む組成物を、酸化物 (Li_2O) 換算で $0.01 \sim 1.0000 \text{ ppm}$ 含有することを特徴とする請求項1または請求項2記載の誘電体磁器組成物。

【請求項5】 前記仮焼き工程で得られた粉末と、 Li の酸化化合物および/または焼成後に Li の酸化化合物となる化合物とを混合する工程を有する誘電体磁器組成物の製造方法。

【請求項6】 前記仮焼き工程で得られた粉末と、 Li の酸化化合物および/または焼成後に Li の酸化化合物となる化合物とを混合する工程を有する誘電体磁器組成物の製造方法。

【請求項7】 誘電体層を有する電子部品であって、前記誘電体層が、

$\left\{ \left(\text{Ba}_{(1-x)} \text{Ca}_x \right) \text{O} \right\} \wedge \left(\text{Ti}_{(1-y)} \text{Zr}_y \right)_B \text{O}_2$ で示される組成の誘電体酸化物を含む主成分と、

$\text{Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si}$ および P の酸化物および/または焼成後にこれらの酸化物になる化合物から選ばれる1種類以上を含む副成分とを有し、

前記副成分が、組成物全体に対して、酸化物換算で、 $0.001 \sim 5$ モル%含まれ、

前記主成分を示す式中の組成比を示す記号 A, B, x, y が、

$0.990 \leq A/B < 1.000$ 、

$0.01 \leq x \leq 0.25$ 、

$0.1 \leq y \leq 0.3$ の関係にある電子部品。

【請求項8】 前記誘電体層が、 Li の酸化化合物および/または焼成後に Li の酸化化合物となる化合物を、酸化物 (Li_2O) 換算で $0.01 \sim 1.0000 \text{ ppm}$ 含有する特徴とする請求項6に記載の電子部品。

【請求項9】 $\text{Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si}$ および P の酸化物および/または焼成後にこれらの酸化物になる化合物から選ばれる1種類以上を含む副成分を含む組成物を、酸化物 (Li_2O) 換算で $0.01 \sim 1.0000 \text{ ppm}$ 含有することを特徴とする請求項1記載の誘電体磁器組成物。

【請求項10】 前記仮焼き工程で得られた粉体と、 $\left\{ \left(\text{Ba}_{(1-x)} \text{Ca}_x \right) \text{O} \right\} \wedge \left(\text{Ti}_{(1-y)} \text{Zr}_y \right)_B \text{O}_2$ で示される組成の誘電体酸化物を含む主成分とを混合する工程と、

混合された粉体を用いて誘電体ペーストを作製する工程と、

【請求項11】 内部電極用ペーストを作製する工程と、前記誘電体ペーストおよび内部電極用ペーストを交互に積層する工程と、

交互に積層された前記誘電体ペーストおよび内部電極用ペーストを焼成する工程とを有する電子部品の製造方法。

【請求項12】 前記仮焼き工程で得られた粉末と、 Li の酸化化合物および/または焼成後に Li の酸化化合物となる化合物とを混合する工程をさらに有する請求項8に記載の電子部品の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、たとえば積層型セラミックコンデンサの誘電体層などとして用いられる誘電体磁器組成物の改良と、その誘電体磁器組成物を誘電体層として用いる電子部品およびそれらの製造方法に関する。

【0002】

【従来の技術】 従来、積層型セラミックコンデンサは、所定の誘電体磁器組成物からなるグリーンシート上に導電ペーストを印刷し、該導電ペーストを印刷した複数枚のグリーンシートを積層し、グリーンシートと内部電極とを一体的に焼成し、形成されている。そして、従来、卑金属を内部電極として用いることができる非還元性誘電体磁器組成物として、例えば、セラミックスコンデンサで高容量材料の特許番号第2787746号で開示されるようものが知られている。

【0003】 この公報に開示される誘電体磁器組成物は、 $\left\{ \left(\text{Ba}_{(1-x)} \text{Ca}_x \right) \text{O} \right\} \wedge \left(\text{Ti}_{(1-y)} \text{Zr}_y \right)_B \text{O}_2$ にて示される誘電体酸化物を主成分とする。ただし、 $1.000 \leq A$

$\sqrt{B} < 1.020$ 、 $0.01 \leq x \leq 0.25$ 、 $0 \leq y \leq 0.05$ 、 $0.05 \leq z \leq 0.20$ である。

【0004】しかしながら、この誘電体磁器組成物では、焼成時に発生する誘電体材料の還元反応を抑えることができるものの、焼成に1220°C以上の高い焼成温度が必要である。

【0005】また、近年、低温焼成が可能な誘電体磁器組成物として、特開平10-279353号公報、特公平6-14496号公報、および特開平4-367559号公報に開示されるようなものが知られている。特公平6-14496号公報には、 $\{(Ba_{(1-x)}Ca_x)_m(Ti_{(1-y-z)}Zr_yR_z)_nO_{2-z/2}$ にて表される主成分と、 SiO_2 、 Li_2O および MO (MO は BaO 等) からなる添加成分との混合物を焼成してなる誘電体磁器組成物が開示されている。ただし、主成分中のRはY等の希土類元素であり、 $1.00 \leq m \leq 1.04$ である。

【0006】この公報には、主成分を1200°Cで仮焼きし、添加成分を1000°Cで仮焼し、主成分と添加成分の仮焼粉末とを混合し、この混合粉末でスラリーを形成し、所定形状に成形し、1150°Cで焼成することにより焼結体が得られることが開示してある。

【0007】また、特開平4-367559号公報には、 $(Ba_{(1-x)}Ca_x)_m(Ti_{(1-y)}Zr_y)_nO_3 + aM1 + bM2 + cM3$ にて表される磁器組成物が開示されている。ただし、M1は Mn 等の化合物、M2は Si の化合物、M3はYの化合物である。

【0008】この公報には、 $BaCO_3$ 、 $CaCO_3$ 、 TiO_2 、 ZrO_2 、 SiO_2 、 Y_2O_3 等の粉末を混合し、この粉末を1050~1240°Cで仮焼し、この仮焼粉末を用いて成形体を作製し、1300~1400°Cで焼成することにより焼結体が得られることが開示されている。これらの誘電体磁器組成物では、還元性雰囲気で焼成しても磁器が還元されず、長寿命のチップコンデンサを得ることができる。

【0009】また、特開平10-279353号公報には、 $\{(Ba_{(1-x)}Ca_x)_m(Ti_{(1-y)}Zr_y)_nO_3\}$ を主成分とし、Y、Li、BまたはSiの酸化物を副成分として含む誘電体磁器組成物が開示されている。ただし、 $0.990 \leq A / B < 1.02$ 、 $0.01 \leq x \leq 0.10$ 、 $0.15 \leq y \leq 0.25$ である。さらに、特開平11-130531号公報には、 $\{(Ba_{(1-x)}Ca_x)_m(Ti_{(1-y)}Zr_y)_nO_3\}$ を主成分とし、Y、Si、BaおよびCaの酸化物を副成分として含む誘電体磁器組成物が開示されている。ただし、 $0.98 \leq A / B < 1.01$ 、 $0.01 \leq x \leq 0.10$ 、 $0.15 \leq y \leq 0.25$ である。

【0010】しかしながら、これらの公報に示す誘電体

磁器組成物では、薄層化の点で問題があると共に、焼成温度が高いなどの課題があった。

【0011】積層型セラミックチップコンデンサは、通常、内部電極用のペーストと、誘電体層用のペーストとをシート法や印刷法等により積層し、一体同時焼成して製造される。内部電極には、一般に、 Pd や Pd 合金が用いられているが、 Pd は高価であるため、比較的安価な Ni や Ni 合金が使用されつつある。ところで、内部電極を Ni や Ni 合金で形成する場合は、大気中で焼成を行うと電極が酸化してしまう。

【0012】このため、一般に、脱バインダ後は、 Ni と NiO の平衡酸素分圧よりも低い酸素分圧で焼成を行っている。この場合、誘電体材料の緻密化を図るために、通常、焼結助剤として SiO_2 が加えられる。また、誘電体層の還元による絶縁抵抗の低下等を防止するため、 Mn の添加や、 Ca 置換等も行われている。

【0013】しかし、 Ni や Ni 合金製の内部電極を有する積層型チップコンデンサは、大気中で焼成して製造される Pd 製の内部電極を有する積層型チップコンデンサに比べて、絶縁抵抗の寿命が圧倒的に短く、信頼性が低いという問題があった。

【0014】ところが、この問題は、本発明者等により提案された、ある特定の組成を有する誘電体酸化物を主成分として含有し、 Y 、 Gd 、 Tb 、 Dy 、 Zr 、 V 、 Mo 、 Zn 、 Cd 、 Ti 、 Sn および P の酸化物および/または焼成後にこれらの酸化物になる化合物から選ばれる1種類以上を特定量添加した誘電体材料と、 Ni または Ni 合金の内部電極材料とを積層して焼成した積層型セラミックチップコンデンサにより、ほぼ解決することができた（特開平3-133116号公報）。すなわち、この公報に示すように、 Y 等を副成分として添加すれば、従来の無添加の誘電体材料を持つチップコンデンサに比べ、寿命が約2~10倍に増大し、ある程度優れた信頼性が得られることが判明した。

【0015】

【発明が解決しようとする課題】しかしながら、上記のような組成の誘電体層を備える積層型セラミックチップコンデンサにおいては、1400°C未満では緻密化しないという問題があり、そこで従来では、焼結助剤として SiO_2 を用いて、上記磁器組成物の低温化焼成を可能としていた。

【0016】しかしながら、従来のように、主成分（ $A / B < 1$ ）に対して、焼結助剤として SiO_2 の比率を多くした場合には、半導体化を生じたり、絶縁抵抗も低く加速寿命も短いという問題があった。

【0017】本発明の目的は、非酸化性雰囲気で1200°C以下の温度での焼成が可能であるにもかかわらず、高い誘電率を有する誘電体磁器組成物およびその製造方法を提供することである。また、本発明の目的は、低温焼成が可能で、しかも絶縁抵抗の加速寿命が向上された

チップコンデンサなどの電子部品を提供することである。

【0018】

【課題を解決するための手段】本発明の発明者等は、積層型セラミックチップコンデンサなどの電子部品の誘電体層として用いられる誘電体磁器組成物において、Y等添加の誘電体磁器組成物に比べ、更に低温での焼成を可能にし、より一層に信頼性を向上させ、しかも、この高信頼性化により、誘電体層を10μm以下の薄層化を可能とする誘電体磁器組成物について鋭意検討した結果、特定組成の誘電体磁器組成物において、組成比の範囲を特定することで、本発明の目的を達成できることを見出し、本発明を完成させるに至った。

【0019】すなわち、本発明に係る誘電体磁器組成物は、 $\{ \{ Ba_{(1-x)} Ca_x \} O \} \wedge (Ti_{(1-y)} Zr_y)_B O_2$ で示される組成の誘電体酸化物を含む主成分と、Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si およびPの酸化物および/または焼成後にこれらの酸化物になる化合物から選ばれる1種類以上を含む副成分とを有し、前記副成分が、組成物全体に対して、酸化物換算で、0.001～5モル%含まれ、前記主成分を示す式中の組成比を示す記号A, B, x, yが、 $0.990 \leq A/B < 1.000$ 、 $0.01 \leq x \leq 0.25$ 、 $0.1 \leq y \leq 0.3$ の関係にあることを特徴とする。

【0020】本発明に係る誘電体磁器組成物において、好ましくは、組成物全体に対して、Liの酸化化合物および/または焼成後にLiの酸化化合物となる化合物を、酸化物($Li_{12}O$)換算で0.01～15モル%含有する。

【0021】本発明に係る誘電体磁器組成物において、好ましくは、焼成後の誘電体磁器組成物が、Liの酸化化合物および/または焼成後にLiの酸化化合物となる化合物を、酸化物($Li_{12}O$)換算で0.01～1000ppm含有する。焼成後の誘電体磁器組成物中のLiの酸化化合物および/または焼成後にLiの酸化化合物となる化合物の含有量は、原子吸光分析などで測定される。

【0022】本発明に係る誘電体磁器組成物の製造方法は、Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si およびPの酸化物および/または焼成後にこれらの酸化物になる化合物から選ばれる1種類以上を含む副成分を示す式中の組成比を示す記号A, B, x, yが、 $0.990 \leq A/B < 1.000$ 、 $0.01 \leq x \leq 0.25$ 、 $0.1 \leq y \leq 0.3$ の関係にあることを特徴とする。

【0023】本発明に係る誘電体磁器組成物の製造方法において、好ましくは、前記副成分とを混合する工程とを有する。

化化合物となる化合物とを混合する工程をさらに有する。

【0024】本発明に係る電子部品は、誘電体層を有する電子部品であって、前記誘電体層が、 $\{ \{ Ba_{(1-x)} Ca_x \} O \} \wedge (Ti_{(1-y)} Zr_y)_B O_2$ で示される組成の誘電体酸化物を含む主成分と、Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si およびPの酸化物および/または焼成後にこれらの酸化物になる化合物

から選ばれる1種類以上を含む副成分とを有し、前記副成分が、組成物全体に対して、酸化物換算で、0.001～5モル%含まれ、前記主成分を示す式中の組成比を示す記号A, B, x, yが、 $0.990 \leq A/B < 1.000$ 、 $0.01 \leq x \leq 0.25$ 、 $0.1 \leq y \leq 0.3$ の関係にあることを特徴とする。

【0025】本発明に係る電子部品において、好ましくは、前記誘電体層が、Liの酸化化合物および/または焼成後にLiの酸化化合物となる化合物を、酸化物($Li_{12}O$)換算で0.01～1000ppm含有する。

【0026】本発明に係る電子部品の製造方法は、Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si およびPの酸化物および/または焼成後にこれらの酸化物になる化合物から選ばれる1種類以上を含む副成分を示す式中の組成比を示す記号A, B, x, yが、 $0.990 \leq A/B < 1.000$ 、 $0.01 \leq x \leq 0.25$ 、 $0.1 \leq y \leq 0.3$ の関係にあることを特徴とする。

【0027】本発明に係る電子部品の製造方法において、好ましくは、前記副成分とを混合する工程と、混合された粉体を用いて誘電体ペーストを作製する工程と、内部電極用ペースト

を作製する工程と、前記誘電体ペーストおよび内部電極用ペーストを交互に積層する工程と、交互に積層された前記誘電体ペーストおよび内部電極用ペーストを焼成する工程とを有する。

【0028】本発明に係る電子部品の製造方法において、好ましくは、前記副成分とを混合する工程と、混合された粉体を用いて誘電体ペーストを作製する工程と、内部電極用ペースト

を作製する工程と、前記誘電体ペーストおよび内部電極用ペーストを交互に積層する工程と、交互に積層された前記誘電体ペーストおよび内部電極用ペーストを焼成する工程とを有する。

【0029】また、本発明に係る誘電体磁器組成物の製造方法では、従来より低温での焼成が可能でありながら、緻密性の高い焼結体が得られる。

【0030】さらに、本発明に係る電子部品の製造方法では、従来より低温での焼成が可能でありながら、緻密

性の高い焼結体から成る誘電体層が得られ、しかも、内部電極の途切れや太りが低減し、長寿命化する効果が得られる。

【0031】

【発明の実施の形態】以下、本発明を、図面に示す実施形態に基づき説明する。図1は本発明の一実施形態に係る積層セラミックコンデンサの要部断面図である。

【0032】積層セラミックコンデンサ

図1に示すように、本発明の一実施形態に係る電子部品としての積層セラミックコンデンサ1は、誘電体層2と内部電極層3とが交互に積層された構成のコンデンサ素子本体10を有する。このコンデンサ素子本体10の両端部には、素子本体10の内部で交互に配置された内部電極層3と各々導通する一対の外部電極4が形成してある。コンデンサ素子本体10の形状に特に制限はないが、通常、直方体状とされる。また、その寸法にも特に制限はなく、用途に応じて適当な寸法とすればよいが、通常、(0.6～5.6mm)×(0.3～5.0mm)×(0.3～1.9mm)程度である。

【0033】内部電極層3は、各端面がコンデンサ素子本体10の対向する2端部の表面に交互に露出するよう積層してある。一対の外部電極4は、コンデンサ素子本体10の両端部に形成され、交互に配置された内部電極層3の露出端面に接続されて、コンデンサ回路を構成する。

【0034】誘電体層2

誘電体層2は、本発明の誘電体磁器組成物を含有する。本発明の誘電体磁器組成物は、 $\left(\left\{Ba_{(1-x)}Ca_x\right\}O\right)_a\left(Ti_{(1-y)}Zr_y\right)_bO$ で表される組成の誘電体酸化物を含む主成分と、Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, SiおよびPの酸化物から選ばれる1種類以上を含む副成分とを有する。この際、酸素(O)量は、上記式の科学量論組成から若干偏倚してもよい。

【0035】上記式中、xは、0.01以上0.25以下、好ましくは0.05以上0.10以下である。また、yは、0.1以上0.3以下、好ましくは0.1以上0.2以下である。また、A/Bは、0.990以上1.000未満、好ましくは0.995以上0.999以下である。

【0036】この組成において、xはCa原子数を表すが、このCaは、主に焼結安定性として作用するとともに、絶縁抵抗値を向上させる元素として作用するものである。xが0.01未満になると、焼成温度が1250°C以上となり絶縁抵抗値が $1 \times 10^7 \Omega$ を下回ることになり、また、xが0.25を超えると、比誘電率が8000を下回り、いずれの場合でも、積層セラミックコンデンサとしての基本特性を満足することができない。従って、xの値は、 $0.01 \leq x \leq 0.25$ の範囲が望ましい。

【0037】前記組成式において、yはZrの原子数を表すが、このZrは、主にキュリ一点を低温側に移動させるシフターとして作用するものである。yが0.1未満となると誘電損失が8%を超てしまい、また、yが0.3を超えると比誘電率が8000を下回り、いずれの場合でも積層セラミックコンデンサとしての基本特性を満足することができない。従って、yの値は0.1 $\leq y \leq 0.3$ の範囲が望ましい。

【0038】前記組成式において、A/Bが0.99未満になると、焼成時に誘電体層の異常粒成長が生じると共に、絶縁抵抗値が $1 \times 10^7 \Omega$ 未満となってしまい、また、A/Bが1.00を超えると焼結性が低下し、緻密な焼結体が得られない。従って、A/Bは0.99 $\leq A/B < 1.00$ の範囲が好ましい。そして、従来の誘電体磁器組成物と異なる点は、A/B < 1 の範囲で副成分を添加することと、Li酸化化合物を添加する点にある。

【0039】このように、副成分を添加することにより、主成分のA/B < 1 の範囲での誘電特性を劣化させることなく低温焼成が可能となり、誘電体層を薄層化した場合の信頼性不良を低減することができ、長寿命化を図ることができるのである。

【0040】本発明では、副成分が組成物の全体に対して0.001モル%未満となると、焼結性が低下し、緻密な焼結体が得られない。また、5モル%を超えると、絶縁抵抗値が $1 \times 10^7 \Omega$ を下回ることになり、積層セラミックコンデンサとしての基本特性を満足することができない。この副成分は、Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, SiおよびPの酸化物および/または焼成後にこれらの酸化物になる化合物から選ばれる1種類以上、好ましくは3種類以上含む。この副成分は、組成物全体に対して、酸化物換算で、0.001～5モル%含まれる。このような副成分を上記モル%範囲で含ませることにより、組成物を焼成して得られる誘電体層を持つセラミックコンデンサの高温負荷寿命が向上する。

【0041】好ましくは、副成分として、マンガンの酸化物および/または焼成により酸化物になる化合物を、酸化物(MnO)換算で0.03～2モル%、好ましくは0.2～1.3モル%、より好ましくは0.2～0.4モル%、イットリウムの酸化物および/または焼成により酸化物になる化合物を、酸化物(Y₂O₃)換算で、0.05～0.5モル%、好ましくは0.08～0.45モル%、より好ましくは0.2～0.4モル%、バナジウムの酸化物および/または焼成により酸化物になる化合物を、酸化物(V₂O₅)換算で、0.005～0.5モル%、好ましくは0.01～0.1モル%、タンクステンの酸化物および/または焼成により酸化物になる化合物を、酸化物(WO₃)換算

で、0.005～0.3モル%、好ましくは0.01～0.2モル%、より好ましくは0.01～0.1モル%程度含有する。このような副成分を上記範囲で含有させることにより、特に低温での焼結性が向上する。また、上記の副成分以外に、Ni酸化物、Nb酸化物、Mg酸化物、Co酸化物、Hf酸化物等が、副成分の合計として、0.5重量%程度以下含有されてもよい。

【0042】また、本発明に係る誘電体磁器組成物では、組成物全体に対して、Liの酸化化合物および／または焼成後にLiの酸化物になる化合物（たとえばLiの珪酸化合物）を、酸化物(Li₂O)換算で、0.01～1.5モル%を、焼結助材として添加してあることが好ましい。

【0043】これらの量が、上記範囲を外れると、誘電体磁器組成物の焼結性が低下すると共に、得られるセラミックコンデンサの電気特性が低下してしまう傾向にある。なお、Li酸化物は、誘電体磁器組成物に対して直接に添加してもよいが、誘電体磁器組成物を、Liを含む雰囲気ガス中で焼成することでも、得られる焼結体中に含有させることができる。ただし、雰囲気ガス中のLiを、酸化物(Li₂O)換算で、0.01～150000ppmで含ませることが好ましい。0.01ppm未満となると焼結性が低下し、緻密な焼結体が得られない。また、150000ppmを超えると、絶縁抵抗値が $1 \times 10^7 \Omega$ を下回ることになり、積層セラミックコンデンサとしての基本特性を満足することができない。

【0044】上記の副成分は、予め、500～1000°Cで仮焼きした後、主成分中に後添加する方法が、低温焼成には望ましく、この副成分とLiの酸化化合物とを、主成分中に後添加する方法が、低温焼成にはさらに望ましい。

【0045】これらの方法により得られた焼成後の誘電体層は、原子吸光分析等で測定した結果、Liを、その酸化物(Li₂O)換算で、好ましくは0.01～10000ppm、さらに好ましくは1～5000、特に好ましくは1～500ppm含有することが好ましい。

【0046】なお、図1に示す誘電体層2の積層数や厚み等の諸条件は、目的や用途に応じ適宜決定すればよい。また、誘電体層2は、グレインと1%以下の粒界相とで構成され、誘電体層2のグレインの平均粒子径は、1～5μm程度あることが好ましい。

【0047】この粒界相は、通常、誘電体材料あるいは内部電極材料を構成する材質の酸化物や、別途添加された材質の酸化物、さらには工程中に不純物として混入する材質の酸化物を成分とし、通常ガラスないしガラス質で構成されている。

【0048】内部電極層3

内部電極層3に含有される導電材は特に限定されないが、誘電体層2の構成材料が耐還元性を有するため、卑

金属を用いることができる。導電材として用いる卑金属としては、NiまたはNi合金が好ましい。Ni合金としては、Mn, Cr, CoおよびAlから選択される1種以上の元素とNiとの合金が好ましく、合金中のNi含有量は95重量%以上であることが好ましい。なお、NiまたはNi合金中には、P, Fe, Mg等の各種微量元素成分が0.1重量%程度以下含まれていてもよい。内部電極層の厚さは用途等に応じて適宜決定すればよいが、通常、0.5～5μm、特に1～2.5μm程度であることが好ましい。

【0049】外部電極4

外部電極4に含有される導電材は特に限定されないが、通常、CuやCu合金あるいはNiやNi合金等を用いる。なお、AgやAg-Pd合金等も、もちろん使用可能である。なお、本実施形態では、安価なNi, Cuや、これらの合金を用いる。外部電極の厚さは用途等に応じて適宜決定されればよいが、通常、10～50μm程度であることが好ましい。

【0050】積層セラミックコンデンサの製造方法

20 本発明の誘電体磁器組成物を用いた積層セラミックコンデンサは、従来の積層セラミックコンデンサと同様に、ペーストを用いた通常の印刷法やシート法によりグリーンチップを作製し、これを焼成した後、外部電極を印刷または転写して焼成することにより製造される。以下、製造方法について具体的に説明する。

【0051】誘電体層用ペーストは、誘電体原料と有機ビヒクルとを混練した有機系の塗料であってもよく、水系の塗料であってもよい。

【0052】誘電体原料には、前述した本発明に係る誘電体磁器組成物の組成に応じ、主成分を構成する原料と、副成分を構成する原料と、必要に応じて焼結助剤を構成する原料とが用いられる。主成分を構成する原料としては、Ti, Ba, Sr, Ca, Zrの酸化物および／または焼成により酸化物になる化合物が用いられる。副成分を構成する原料としては、Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, SiおよびPの酸化物および／または焼成により酸化物になる化合物から選ばれる1種類以上、好ましくは3種類以上の単一酸化物または複合酸化物が用いられる。焼結助剤を構成する原料としては、Liの酸化物および／または焼成により酸化物になる化合物が用いられる。焼成により酸化物になる化合物としては、例えば炭酸塩、硝酸塩、シウ酸塩、有機金属化合物等が例示される。もちろん、酸化物と、焼成により酸化物になる化合物とを併用してもよい。

【0053】これらの原料粉末は、通常、平均粒子径0.0005～5μm程度のものが用いられる。このような原料粉末から誘電体材料を得るには例えば下記のようにすればよい。

【0054】まず、出発原料を所定の量比に配合し、例

えば、ボールミル等により湿式混合する。次いで、スプレードライヤー等により乾燥させ、その後仮焼し、主成分を構成する上記式の誘電体酸化物を得る。なお、仮焼は、通常500～1300℃、好ましくは500～1000℃、さらに好ましくは800～1000℃にて、2～10時間程度、空気中にて行う。次いで、ジェットミルあるいはボールミル等にて所定粒径となるまで粉碎し、誘電体材料を得る。副成分と、焼結助剤(SiO₂またはLi₂Oなど)とは、それぞれ主成分とは別に仮焼きし、得られた誘電体材料に混合される。この主成分の仮焼き時に、副成分も含めて行うと所望の特性が得られない。また、副成分とLi₂Oとを含めて行う仮焼きも低温焼成の効果を半減させる。副成分とLi₂Oとを同時に仮焼きすると、Li化合物を生成し、主成分との反応が著しく低下、あるいは焼成温度が高くなる。

【0055】誘電体層用ペーストを調整する際に用いられる結合剤、可塑剤、分散剤、溶剤等の添加剤は種々のものであつてよい。また、誘電体層用のペーストにはガラスフリットを添加してもよい。結合剤としては、例えばエチルセルロース、アビエチン酸レジン、ポリビニール・ブチラールなど、可塑剤としては、例えばアビエチン酸誘導体、ジエチル蔥酸、ポリエチレングリコール、ポリアルキレングリコール、フタル酸エステル、フタル酸ジブチルなど、分散剤としては、例えばグリセリン、オクタデシルアミン、トリクロロ酢酸、オレイン酸、オクタジエン、オレイン酸エチル、モノオレイン酸グリセリン、トリオレイン酸グリセリン、トリステアリン酸グリセリン、メンセーデン油など、溶剤としては、例えばトルエン、テルピネオール、ブチルカルビトール、メチルエチルケトンなどが挙げられる。このペーストを焼成する際に、誘電体材料がペースト全体に対して占める割合は50～80重量%程度とし、その他、結合剤は2～5重量%、可塑剤は0.01～5重量%、分散剤は0.01～5重量%、溶剤は20～50重量%程度とする。そして、前記誘電体材料とこれら溶剤などを混合し、例えば3本ロール等で混練してペースト(スラリー)とする。

【0056】なお、誘電体層用ペーストを水系の塗料とする場合には、水溶性のバインダや分散剤などを水に溶解させた水系ビヒクルと、誘電体原料とを混練すればよい。水系ビヒクルに用いる水溶性バインダは特に限定されず、例えば、ポリビニルアルコール、セルロース、水溶性アクリル樹脂などを用いればよい。

【0057】内部電極層用ペーストは、各種導電性金属や合金からなる導電体材料、あるいは焼成後に上記した導電体材料となる各種酸化物、有機金属化合物、レジネート等と、有機ビヒクルとを混練して調製する。

【0058】内部電極用のペーストを製造する際に用いる導電体材料としては、NiやNi合金さらにはこれらの

混合物を用いる。このような導電体材料は、球状、リン片状等、その形状に特に制限はなく、また、これらの形状のものが混合したものであつてもよい。また、導電体材料の平均粒子径は、通常、0.1～10μm、好ましくは0.1～1μm程度のものを用いればよい。

【0059】有機ビヒクルは、バインダーおよび溶剤を含有するものである。バインダーとしては、例えばエチルセルロース、アクリル樹脂、ブチラール樹脂等公知のものはいずれも使用可能である。バインダー含有量は1～5重量%程度とする。溶剤としては、例えばテルピネオール、ブチルカルビトール、ケロシン等公知のものはいずれも使用可能である。溶剤含有量は、ペースト全体に対して、20～55重量%程度とする。

【0060】このようにして得られた内部電極層用ペーストと誘電体層用ペーストとは、印刷法、転写法、グリーンシート法等により、それぞれ交互に積層される。印刷法を用いる場合、誘電体層用ペーストおよび内部電極層用ペーストを、PET等の基板上に積層印刷し、所定形状に切断した後、基板から剥離して積層体とする。また、シート法を用いる場合、誘電体層用ペーストを用いてグリーンシートを形成し、この上に内部電極層用ペーストを印刷した後、これらを積層して積層体とする。

【0061】次に、このようにして得られた積層体を、所定の積層体サイズに切断した後、脱バインダ処理および焼成を行う。そして、誘電体層2を再酸化させるため、熱処理を行う。

【0062】脱バインダ処理は、通常の条件で行えばよいが、内部電極層の導電体材料にNiやNi合金等の卑金属を用いる場合、特に下記の条件で行うことが好ましい。

昇温速度：5～300℃/時間、特に10～50℃/時間、
保持温度：200～400℃、特に250～350℃、
保持時間：0.5～20時間、特に1～10時間、
雰囲気：空気中。

【0063】焼成条件は、下記の条件が好ましい。
昇温速度：50～500℃/時間、特に200～300℃/時間、
保持温度：1000～1200℃、特に1100～1200℃、

保持時間：0.5～8時間、特に1～3時間、
冷却速度：50～500℃/時間、特に200～300℃/時間、
雰囲気ガス：加湿したN₂とH₂との混合ガス等。

【0064】ただし、焼成時の空気雰囲気中の酸素分圧は、10⁻⁷atm以下、特に10⁻⁷～10⁻¹³atmにて行うことが好ましい。前記範囲を超えると、内部電極層が酸化する傾向にあり、また、酸素分圧があまり低すぎると、内部電極層の電極材料が異常焼結を起こし、途切れてしまう傾向にある。

【0065】焼成後の熱処理は、保持温度または最高温度を900～1100℃として行うことが好ましい。熱処理時の保持温度または最高温度が、前記範囲未満では誘電体材料の酸化が不十分なために寿命が短くなる傾向にあり、前記範囲をこえると内部電極のNiが酸化し、容量が低下するだけでなく、誘電体素地と反応してしまい、寿命も短くなる傾向にある。熱処理の際の酸素分圧は、 10^{-8} atm以上、より好ましくは 10^{-4} ～ 10^{-7} atmが好ましい。前記範囲未満では、誘電体層2の再酸化が困難であり、前記範囲をこえると内部電極層3が酸化する傾向にある。そして、そのほかの熱処理条件は下記の条件が好ましい。

【0066】保持時間：0～6時間、特に2～5時間、冷却速度：50～500℃/時間、特に100～300℃/時間、

雰囲気用ガス：加湿したN₂ガス等。

【0067】なお、N₂ガスや混合ガス等を加湿するには、例えばウェッター等を使用すればよい。この場合、水温は0～75℃程度が好ましい。また脱バインダ処理、焼成および熱処理は、それぞれを連続して行っても、独立に行ってもよい。これらを連続して行なう場合、脱バインダ処理後、冷却せずに雰囲気を変更し、続いて焼成の際の保持温度まで昇温して焼成を行ない、次いで冷却し、熱処理の保持温度に達したときに雰囲気を変更して熱処理を行なうことが好ましい。一方、これらを独立して行なう場合、焼成に際しては、脱バインダ処理時の保持温度までN₂ガスあるいは加湿したN₂ガス雰囲気下で昇温した後、雰囲気を変更してさらに昇温を続けることが好ましく、アニール時の保持温度まで冷却した後は、再びN₂ガスあるいは加湿したN₂ガス雰囲気に変更して冷却を続けることが好ましい。また、アニールに際しては、N₂ガス雰囲気下で保持温度まで昇温した後、雰囲気を変更してもよく、アニールの全過程を加湿したN₂ガス雰囲気としてもよい。

【0068】このようにして得られた焼結体には、例えばバーレル研磨、サンドブラスト等にて端面研磨を施し、外部電極用ペーストを焼きつけて外部電極4を形成する。外部電極用ペーストの焼成条件は、例えば、加湿したN₂とH₂との混合ガス中で600～800℃にて10分間～1時間程度とすることが好ましい。そして、必要に応じ、外部電極4上にめっき等を行うことによりパッド層を形成する。なお、外部電極用ペースト

は、上記した内部電極層用ペーストと同様にして調製すればよい。

【0069】このようにして製造された本発明の積層セラミックコンデンサは、ハンダ付等によりプリント基板上などに実装され、各種電子機器等に使用される。

【0070】なお、本発明は、上述した実施形態に限定されるものではなく、本発明の範囲内で種々に改変することができる。たとえば、上述した実施形態では、本発明に係る電子部品として積層セラミックコンデンサを例示したが、本発明に係る電子部品としては、積層セラミックコンデンサに限定されず、上記組成の誘電体磁器組成物で構成してある誘電体層を有するものであれば何でも良い。

【0071】

【実施例】以下、本発明を、さらに詳細な実施例に基づき説明するが、本発明は、これら実施例に限定されない。

【0072】実施例1

出発原料として、ゾルゲル合成により生成された{(B_a_(1-x)Ca_x)O}_A·(Ti_(1-y)Zr_y)_BO₂で示される組成の誘電体酸化物から成る主成分を用いた。主成分を示す式中の組成比を示す記号A, B, x, yが、0.990≤A/B<1.000、0.01≤x≤0.25、0.1≤y≤0.3の関係の関係にあった。なお、上記誘電体酸化物の平均粒径は、0.4μm、最大粒径は1.5μmであった。

【0073】また、副成分であるMnCO₃、Y₂O₃、V₂O₅およびWO₃とSiO₂とを、添加物(添加物全体の平均粒径0.5μm、最大粒径3.3)として、表1に示すモル比にて、各々ボーラルミルで16時間湿式粉碎し、900℃および3時間の条件で、大気雰囲気中で仮焼きし、その後、解碎のためにボーラルミルで20時間湿式粉碎し、副成分の添加物とした。そして、主成分と副成分とLi₂CO₃を、ボーラルミルで16時間、湿式粉碎し、表1に示す試料番号1～34のチタン酸バリウム系の誘電体材料を得た。また、副成分にLi₂CO₃も加えて仮焼きした以外は、前記と同様の方法で、表1に示す試料番号35のチタン酸バリウム系の誘電体材料を得た。

【0074】

【表1】

試料No.	A/B	主成分 (モル)		含有量 (モル)					後添加 (mol%)
		X	Y	MnO	Ta ₂ O ₅	VO ₂	WO ₃	SiO ₂	
1	1.000	0.08	0.20	0.372	0.111	0.06	0.037	0.59	0
2	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	0
3	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	0.05
4	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	0.3
5	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	1
6	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	5
7	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	15
8	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	25
9	0.997	0.08	0.20	0.35	0.259	0.059	0.034	0	0
10*	0.997	0.08	0.20	0.348	0.252	0.055	0.034	0	0.05
11*	0.997	0.08	0.20	0.348	0.252	0.055	0.034	0	0.3
12*	0.997	0.08	0.20	0.348	0.252	0.055	0.034	0	1
13*	0.997	0.08	0.20	0.348	0.252	0.055	0.034	0	5
14*	0.997	0.08	0.20	0.348	0.252	0.055	0.034	0	15
15	0.997	0.08	0.20	0.348	0.252	0.055	0.034	0	25
16*	0.991	0.08	0.21	0.352	0.259	0.04	0.034	0	3
17*	0.997	0.08	0.21	0.351	0.258	0.05	0.035	1.122	0.3
18*	0.999	0.08	0.20	0.352	0.255	0.044	0.037	0.753	1
19*	0.997	0.08	0.18	0.348	0.259	0.04	0.034	1.804	1
20	0.990	0.078	0.204	0.353	0.283	0.047	0.038	0.8	1
21	0.985	0.077	0.202	0.351	0.284	0.047	0.037	0.8	1
22	0.987	0.077	0.203	0.352	0.278	0.044	0.037	0.3	1
23	0.989	0.078	0.203	0.349	0.288	0.04	0.037	0.422	0.05
24	0.989	0.078	0.203	0.349	0.288	0.04	0.037	0.422	0.3
25	0.989	0.078	0.203	0.349	0.288	0.04	0.037	0.422	1
26	0.989	0.078	0.203	0.349	0.288	0.04	0.037	0.422	5
27	0.989	0.078	0.203	0.348	0.288	0.04	0.037	0.422	15
28	0.989	0.078	0.203	0.348	0.288	0.04	0.037	0.422	25
29	0.997	0.08	0.20	0.8	0.14	0.01	0.01	0.8	0.3
30	0.997	0.09	0.20	0.3	0.2	0.055	0.034	0.8	0.3
31	0.997	0.09	0.20	0.4	0.3	0.055	0.034	0.36	0.3
32	0.997	0.09	0.20	0.5	0.3	0.055	0.034	0.5	0.3
33	0.997	0.09	0.20	0.4	0.2	0.01	0.01	0.3	0.3
34	0.997	0.09	0.20	0.4	0.2	0.01	0.034	0	0.3
35	0.990	0.05	0.20	0.2	0.2	0.06	0.03	0.8	0.2

【0075】これら試料番号1～35の誘電体材料の各々を用いて、下記に示される配合比にて、ジルコニア製ボールを用いてボールミル混合し、スラリー化して誘電体層用ペーストとした。すなわち、誘電体材料：100重量部、アクリル系樹脂：5.0重量部、フタル酸ベンジルブチル：2.5重量部、ミネラルスピリット：6.5重量部、アセトン：4.0重量部、トリクロロエタン：20.5重量部、塩化メチレン：41.5重量部の配合比である。

【0076】次に、下記に示される配合比にて、3本ロールにより混練し、スラリー化して内部電極用ペーストとした。すなわち、Ni：44.6重量部、テルピネオール：52重量部、エチルセルロース：3重量部、ベンゾトリアゾール：0.4重量部である。これらのペーストを用い、以下のようにして、図1に示される積層型セラミックチップコンデンサ1を製造した。

【0077】まず、誘電体層用ペーストを用いてキャリ

アフィルム上に16μm厚のシートを、ドクターブレード法などで形成し、この上に内部電極用ペーストを用いて、内部電極を印刷した。この後、キャリヤフィルムから上記のシートを剥離し、内部電極が印されたシートを複数枚積層し、加圧接着した。なお、誘電体層2の積層数は10層であった。次いで、積層体を所定サイズに切断した後、脱バインダ処理、焼成および熱処理を連続して下記の条件にて行った。

【0078】脱バインダ処理

昇温速度：20℃/時間、

保持温度：250℃、

保持時間：2時間、

雰囲気用ガス：air。

【0079】焼成

昇温速度：200℃/時間、

保持温度：各々、表2に示す温度、

保持時間：2時間、

冷却温度: 300°C/時間、
雰囲気用ガス: 加湿したN₂ と H₂ の混合ガス、
酸素分圧: 10⁻⁸ atm。

【0080】熱処理

保持温度: 1000°C、

保持時間: 3時間、

冷却温度: 300°C/時間、

雰囲気用ガス: 加湿したN₂ ガス、

酸素分圧: 10⁻⁷ atm。

【0081】なお、それぞれの雰囲気用ガスの加湿には、ウェッターを用い、水温0~75°Cにて行った。

【0082】得られた焼結体の端面をサンドブラストにて研磨した後、In-Ga合金を塗布して、試験用電極を形成した。このようにして製造した積層型コンデンサ1のサイズは、3.2mm×1.6mm×0.6mmであり、誘電体層2の厚みは10μm、内部電極3の厚みは2μmであった。

【0083】この積層型コンデンサの特性を、基準温度25°CでデジタルLCRメータ(YHP製4274A)にて、周波数1kHz、測定電圧1.0Vrmsの信号を入力し、静電容量および誘電損失tanδを測定した。誘電体磁器の比誘電率ε_rは、積層型コンデンサの誘電体磁器の試料寸法と静電容量を考慮して算出した。

【0084】なお、絶縁抵抗値は、積層型コンデンサに10Vの直流電圧を1分間印加して測定した。また、破壊電圧は、3V/Sで昇圧し、100mA以上の電流が

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流れた電圧を測定した。評価として、比誘電率ε_rは、小型で高誘電率のコンデンサを作成するために重要な特性であり、8000以上を良好とした。誘電損失tanδは、誘電体層2の薄膜化を実現し、小型で高誘電率のコンデンサを作成するために重要な特性であり、8%以下を良好とした。絶縁抵抗値は1×10⁷ Ω以上を良好とした。破壊電圧は、100V(7V/μm)以上を良好とした。また、これらの特性値は、コンデンサの試料数n=10個を用いて測定した値の平均値から求めた。

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【0085】また、コンデンサの高温負荷寿命(絶縁抵抗の加速寿命)を、200°Cで8V/μmの直流電圧の印加状態に保持することにより測定した。この高温負荷寿命は、10個の積層型コンデンサ試料について行い、最初にショートしたコンデンサの、印加開始からショートに至るまでの時間を測定することにより評価した。高温負荷寿命は、誘電体層を薄層化する際に特に重要なものであり、印加開始からショートに至るまでの時間が40時間以上を良品とした。

【0086】また、各コンデンサ試料における誘電体層中のLiの含有量を、Li₂O換算で、原子吸光分析にて測定した。さらに、コンデンサ試料を切断し、内部電極の途切れがあるか否かを観察した。これらの結果を表2に示した。

【0087】

【表2】

試料No.	焼成温度 (°C)	比誘電率	誘電損失 (%)	絶縁抵抗 IR (Ω)	破壊電圧 (V)	絶縁抵抗 高溫負荷 寿命 (h)	焼成後の 残存量 (ppm)	電極の途切れ (\square ○、 \times)	
								\square ○	\times
1	1250	12000	6	1.00E+10	428.6	30	0	\times	
2	1250	緻密な焼結体得られず	-	-	-	-	0	-	
3	1250	緻密な焼結体得られず	-	-	-	-	5	-	
4	1250	7000	4	1.00E+09	-	-	13	\times	
5	1250	6500	5	1.00E+09	-	-	76	\times	
6	1250	5400	6	1.00E+09	-	-	143	\times	
7	1250	2000	4	1.00E+09	-	-	423	\times	
8	1250	1500	7	1.00E+09	-	-	800	\times	
9	1250	500	30	1.00E+08	-	-	0	\times	
10*	1200	12000	4	1.00E+10	563	200	13	\circ	
11*	1200	12000	4	1.00E+10	547	180	144	\circ	
12*	1180	14000	8	1.00E+10	493	140	312	\circ	
13*	1140	12000	6	1.00E+09	547	120	1633	\circ	
14*	1100	10000	8	1.00E+09	483.3	110	6700	\circ	
15	1050	7000	8	1.00E+08	566	144	18170	\circ	
16*	1140	11000	4	1.00E+10	125	250	1248	\circ	
17*	1140	12000	5	1.00E+10	110	220	139	\circ	
18*	1180	14000	5	1.00E+10	561	220	404	\circ	
19*	1140	12500	5	1.00E+10	489.8	200	453	\circ	
20	1100	8000	10	1.00E+09	644	400	484	\circ	
21	1050	異常粒成長	-	-	-	-	472	-	
22	1200	異常粒成長	-	-	-	-	444	-	
23	1100	異常粒成長	-	-	-	-	14	-	
24	1100	異常粒成長	-	-	-	-	28	-	
25	1050	異常粒成長	-	-	-	-	167	-	
26	1050	異常粒成長	-	-	-	-	907	-	
27	1050	異常粒成長	-	-	-	-	2077	-	
28	1000	異常粒成長	-	-	-	-	31541	-	
29	1140	10000	5.5	1.00E+09	483.3	250	848	\circ	
30*	1140	12000	4	1.00E+10	455	180	187	\circ	
31	1180	14000	6	1.00E+10	655	84	180	\circ	
32	1180	12000	6	1.00E+10	485	104	174	\circ	
33	1200	10000	8	1.00E+09	483.3	108	201	\circ	
34	1190	8000	8	1.00E+08	566	108	197	\circ	
35	1250	8000	4.3	2.80E+10	423	40	118	\times	

【0088】表1および表2において、本発明の特に好みの実施例に相当する試料番号には、*印を付けた。

表1および表2から分かるように、本発明の積層型セラミックチップコンデンサは、焼結助剤としてLi₂Oを用いたことにより、1140°Cという低温で焼成しても、比誘電率ε_rが8000以上となった。また、焼結助剤としてのLi₂Oを添加していないもの（試料番号2および3）は、緻密な焼結体が得られていないことから、本発明の積層型セラミックチップコンデンサは、低温での焼結性が向上していることが分かる。

【0089】副成分の仮焼き温度について、別に実験したところ、1200°C以上の高温で焼成すると副成分の解碎が困難になり、不適正であることが判明した。

【0090】また、試料番号35のように、副成分とLi_iとを同時に予め仮焼きすると、低温焼成の効果が激減することが確認された。副成分とLi_iとを同時に予め仮焼きすると、試料番号35と試料番号20とを比較して分かるように、近い組成でも、焼成温度が100°C以上

に上昇し、電極の途切れも観察されることが確認された。

【0091】

【発明の効果】以上説明してきたように、本発明によれば、非酸化性雰囲気で1200°C以下の温度での焼成が可能であるにもかかわらず、高い誘電率を有する誘電体磁器組成物およびその製造方法を提供することができる。また、本発明によれば、低温焼成が可能で、しかも絶縁抵抗の加速寿命が向上されたチップコンデンサなどの電子部品を提供することができる。

【図面の簡単な説明】

【図1】図1は本発明の一実施形態に係る積層セラミックコンデンサの断面図である。

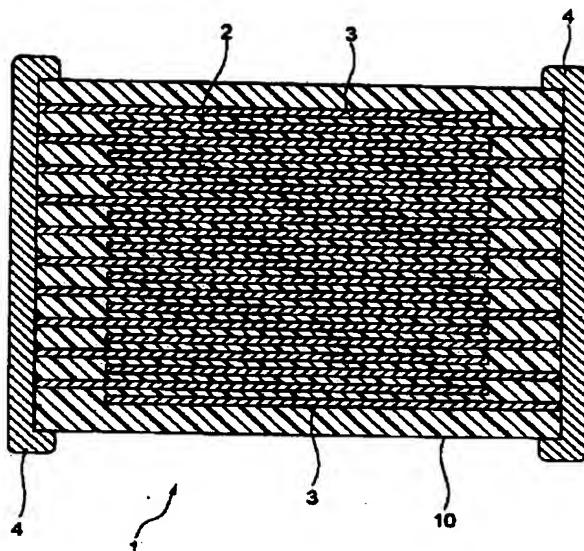
【符号の説明】

- 1…積層セラミックコンデンサ
- 10…コンデンサ素子本体
- 2…誘電体層
- 3…内部電極層

4 …外部電極

【図1】

図 1



フロントページの続き

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CLAIMS

[Claim(s)]

[Claim 1] $\{\{Ba(1-x) Cax []\} O\} A (Ti(1-y) Zry) B O2$ The principal component containing the dielectric oxide of the presentation shown, It has an accessory constituent including one or more kinds chosen from the compound which turns into these oxides after the oxide of Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P, and/or baking. said accessory constituent -- the constituent whole -- receiving -- oxide conversion -- 0.001-5-mol % -- the dielectric porcelain constituent the notations A, Bx, and y which show the presentation ratio in the formula in which being contained in and showing said principal component have the relation of $0.990 \leq A/B \leq 1.000$, $0.01 \leq x \leq 0.25$, and $0.1 \leq y \leq 0.3$.

[Claim 2] the compound which turns into an oxidation compound of Li after the oxidation compound of Li, and/or baking to the whole constituent -- oxide ($Li_2 O$) conversion -- 0.01-15-mol % -- the dielectric porcelain constituent according to claim 1 characterized by containing.

[Claim 3] The dielectric porcelain constituent according to claim 1 or 2 with which the dielectric porcelain constituent after baking is characterized [which is contained 0.01-10000 ppm by oxide ($Li_2 O$) conversion] by the oxidation compound of Li, and the becoming compound after the oxidation compound of Li, and/or baking.

[Claim 4] The process which carries out temporary baking of the accessory constituent including one or more kinds chosen from the compound which turns into these oxides after the oxide of Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P, and/or baking at 500-1000 degrees C beforehand, The fine particles obtained by this temporary baking, and $\{\{Ba(1-x) Cax []\} O\} A (Ti(1-y) Zry) B O2$ The manufacture approach of a dielectric porcelain constituent of having the process which mixes the principal component containing the dielectric oxide of the presentation shown.

[Claim 5] The manufacture approach of a dielectric porcelain constituent according to claim 4 of having further the process which mixes the oxidation compound of Li, and the becoming compound after the powder obtained at said temporary baking process, the oxidation compound of Li, and/or baking.

[Claim 6] It is the electronic parts which have a dielectric layer, and said dielectric layer is $\{\{Ba(1-x) Cax []\} O\} A (Ti(1-y) Zry) B O2$ The principal component containing the dielectric oxide of the presentation shown, It has an accessory constituent including one or more kinds chosen from the compound which turns into these oxides after the oxide of Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P, and/or baking. said accessory constituent -- the constituent whole -- receiving -- oxide conversion -- 0.001-5-mol % -- the electronic parts the notations A, Bx, and y which show the presentation ratio in the formula in which being contained in and showing said principal component have the relation of $0.990 \leq A/B \leq 1.000$, $0.01 \leq x \leq 0.25$, and $0.1 \leq y \leq 0.3$.

[Claim 7] Electronic parts according to claim 6 with which said dielectric layer is characterized [which is contained 0.01-10000 ppm by oxide ($Li_2 O$) conversion] by the oxidation compound of Li, and the becoming compound after the oxidation compound of Li, and/or baking.

[Claim 8] The process which carries out temporary baking of the accessory constituent including one or more kinds chosen from the compound which turns into these oxides after the oxide of Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P, and/or baking at 500-1000 degrees C beforehand, The fine

particles obtained by this temporary baking, and $\{ \{ \text{Ba}(1-x) \text{Ca}x \text{O} \} \text{A} (\text{Ti}(1-y) \text{Zr}y) \text{B} \text{O}_2$ The process which mixes the principal component containing the dielectric oxide of the presentation shown, The process which produces a dielectric paste using the mixed fine particles, and the process which produces the paste for internal electrodes, The manufacture approach of electronic parts of having the process which carries out the laminating of said dielectric paste and the paste for internal electrodes by turns, and the process which calcinates said dielectric paste and the paste for internal electrodes by which the laminating was carried out by turns.

[Claim 9] The manufacture approach of electronic parts according to claim 8 of having further the process which mixes the oxidation compound of Li, and the becoming compound after the powder obtained at said temporary baking process, the oxidation compound of Li, and/or baking.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to amelioration, the electronic parts using the dielectric porcelain constituent as a dielectric layer, and those manufacture approaches of the dielectric porcelain constituent used as a dielectric layer of for example, a laminating mold ceramic condenser etc.

[0002]

[Description of the Prior Art] Conventionally, a laminating mold ceramic condenser carries out the laminating of the green sheet of two or more sheets which printed conductive paste on the green sheet which consists of a predetermined dielectric porcelain constituent, and printed this conductive paste, calcinates a green sheet and an internal electrode in one, and is formed. And what is indicated by the patent number No. 2787746 of a high capacity ingredient for example, by the ceramic capacitor is conventionally known as a nonreducible dielectric porcelain constituent which can use base metal as an internal electrode.

[0003] The dielectric porcelain constituent indicated by this official report is $\{(Ba(1-x) Cax Sry) O\} A. (Ti(1-z) Zrz) B O2$ Let the dielectric oxide shown be a principal component. However, it is $1.00 \leq A/B < 1.020$, $0.01 \leq x \leq 0.25$, $0 \leq y \leq 0.05$, and $0.05 \leq z \leq 0.20$.

[0004] However, in this dielectric porcelain constituent, a high burning temperature of 1220 degrees C or more is required for baking of what can suppress the reduction reaction of the dielectric materials generated at the time of baking.

[0005] Moreover, what is indicated by JP,10-279353,A, JP,6-14496,B, and JP,4-367559,A is known in recent years as a dielectric porcelain constituent in which low-temperature baking is possible. In JP,6-14496,B, it is $\{(Ba(1-x) Cax) O\} m. (Ti(1-y-z) Zry Rz) O2-z/2$ The principal component with which it is expressed, and $SiO2 Li2$ The dielectric porcelain constituent which comes to calcinate mixture with the addition component which consists of O and MO (MO is BaO etc.) is indicated. However, R in a principal component is rare earth elements, such as Y, and is $1.00 \leq m \leq 1.04$.

[0006] Temporary baking of the principal component is carried out at 1200 degrees C, temporary quenching of the addition component is carried out to this official report at 1000 degrees C, the temporary-quenching powder of a principal component and an addition component is mixed, a slurry is formed with this mixed powder, and it fabricates in a predetermined configuration, and has indicated that a sintered compact is obtained by calcinating at 1150 degrees C.

[0007] Moreover, in JP,4-367559,A, it is $m(Ba(1-x) Cax) (Ti(1-y) Zry) n. O3$ The porcelain constituent expressed with $+aM1+bM2+cM3$ is indicated. However, as for compounds, such as Mn, and M2, M1 is [the compound of Si and M3] the compounds of Y.

[0008] this official report -- $BaCO3 CaCO3 TiO2 ZrO2 SiO2 Y2 O3$ etc. -- powder is mixed, temporary quenching of this powder is carried out at 1050-1240 degrees C, a Plastic solid is produced using this temporary-quenching powder, and it is indicated by calcinating at 1300-1400 degrees C that a sintered compact is obtained. In these dielectric porcelain constituents, even if it calcinates by the reducing atmosphere, porcelain is not returned, but a long lasting chip capacitor can be obtained.

[0009] Moreover, in JP,10-279353,A, it is $\{(Ba(1-x)Cax)O\} A. (Ti(1-y)Zry) B O_3$ It considers as a principal component and the dielectric porcelain constituent which contains the oxide of Y, Li, B, or Si as an accessory constituent is indicated. However, it is $0.990 \leq A/B < 1.02$, $0.01 \leq x \leq 0.10$, and $0.15 \leq y \leq 0.25$. Furthermore, in JP,11-130531,A, it is $\{(Ba(1-x)Cax)O\} A. (Ti(1-y)Zry) B O_3$ It considers as a principal component and the dielectric porcelain constituent which contains the oxide of Y, Si, Ba, and calcium as an accessory constituent is indicated. However, it is $0.98 \leq A/B < 1.01$, $0.01 \leq x \leq 0.10$, and $0.15 \leq y \leq 0.25$.

[0010] However, in the dielectric porcelain constituent shown in these official reports, while there was a problem in respect of lamination, technical problems, like burning temperature is high occurred.

[0011] A laminating mold ceramic chip capacitor carries out the laminating of the paste for internal electrodes, and the paste for dielectric layers by the sheet method, print processes, etc., really carries out coincidence baking, and is usually manufactured. Generally, although Pd and Pd alloy are used, since Pd is expensive, comparatively cheap nickel and nickel alloy are being used for an internal electrode. By the way, when forming an internal electrode with nickel or nickel alloy, if it calcinates in atmospheric air, an electrode will oxidize.

[0012] For this reason, generally after the debinder is calcinating by oxygen tension lower than the balanced oxygen tension of nickel and NiO. In this case, in order to attain eburnation of dielectric materials, it is usually SiO_2 as sintering acid. It is added. Moreover, in order to prevent the fall of the insulation resistance by reduction of a dielectric layer etc., addition, calcium permutation, etc. of Mn are performed.

[0013] However, compared with the laminating mold chip capacitor which has the internal electrode made from Pd calcinated and manufactured in atmospheric air, the laminating mold chip capacitor which has an internal electrode made from nickel or nickel alloy had the overwhelmingly short life of insulation resistance, and had the problem of being unreliable.

[0014] However, this problem contains the dielectric oxide which was proposed by this invention person etc. and which has a certain specific presentation as a principal component. The dielectric materials which carried out the amount addition of specification of the one or more kinds chosen from the compound which turns into these oxides after the oxide of Y, Gd, Tb, Dy, Zr, V, Mo, Zn, Cd, Ti, Sn, and P, and/or baking, It was mostly solvable with the laminating mold ceramic chip capacitor which carried out the laminating of the internal electrode material of nickel or nickel alloy, and calcinated it (JP,3-133116,A). That is, as shown in this official report, when adding Y etc. as an accessory constituent, compared with the chip capacitor with the conventional additive-free dielectric materials, the life increased by about 2 to 10 times, and it became clear that the dependability which was excellent to some extent was acquired.

[0015]

[Problem(s) to be Solved by the Invention] However, in a laminating mold ceramic chip capacitor equipped with the dielectric layer of the above presentations, there is a problem that eburnation is not carried out at less than 1400 degrees C, and it is SiO_2 as sintering acid at the former there. It used and low temperature-ized baking of the above-mentioned porcelain constituent was enabled.

[0016] However, it is [as opposed to / like before / a principal component ($A/B < 1$)] SiO_2 as sintering acid. When a ratio was made [many], semi-conductor-ization was produced and there was a problem that insulation resistance was also low and accelerated aging was also short.

[0017] The purpose of this invention is offering the dielectric porcelain constituent which has a high dielectric constant, and its manufacture approach by the non-oxidizing atmosphere, although baking at the temperature of 1200 degrees C or less is possible. Moreover, low-temperature baking is possible for the purpose of this invention, and it is offering electronic parts, such as a chip capacitor whose accelerated aging of insulation resistance moreover improved.

[0018]

[Means for Solving the Problem] In the dielectric porcelain constituent with which the artificer of this invention etc. is used as a dielectric layer of electronic parts, such as a laminating mold ceramic chip capacitor Compared with the dielectric porcelain constituent of addition, such as Y, baking at low

temperature is enabled further and dependability is raised more to one layer. Moreover, by this high-reliability-ization As a result of examining wholeheartedly the dielectric porcelain constituent which makes lamination 10 micrometers or less possible for a dielectric layer, in the dielectric porcelain constituent of a specific presentation, it came to complete a header and this invention for the ability of the purpose of this invention to be attained by pinpointing the range of a presentation ratio.

[0019] Namely, the dielectric porcelain constituent concerning this invention $\{\{Ba(1-x)Cax\}O\}A(Ti(1-y)Zry)B O2$ The principal component containing the dielectric oxide of the presentation shown, It has an accessory constituent including one or more kinds chosen from the compound which turns into these oxides after the oxide of Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P, and/or baking. said accessory constituent -- the constituent whole -- receiving -- oxide conversion -- 0.001-5-mol % -- it is contained and the notations A, Bx, and y which show the presentation ratio in the formula showing said principal component are characterized by having the relation of $0.990 \leq A/B < 1.000$, $0.01 \leq x \leq 0.25$, and $0.1 \leq y \leq 0.3$.

[0020] the compound which turns into an oxidation compound of Li after the oxidation compound of Li, and/or baking to the whole constituent preferably in the dielectric porcelain constituent concerning this invention -- oxide (Li_2O) conversion -- 0.01-15-mol % -- it contains.

[0021] In the dielectric porcelain constituent concerning this invention, the dielectric porcelain constituent after baking contains the oxidation compound of Li, and 0.01-10000 ppm of becoming compounds by oxide (Li_2O) conversion after the oxidation compound of Li, and/or baking preferably. The content of the oxidation compound of Li and the becoming compound is measured by atomic absorption analysis etc. after the oxidation compound of Li in the dielectric porcelain constituent after baking, and/or baking.

[0022] The manufacture approach of the dielectric porcelain constituent concerning this invention The process which carries out temporary baking of the accessory constituent including one or more kinds chosen from the compound which turns into these oxides after the oxide of Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P, and/or baking at 500-1000 degrees C beforehand, The fine particles obtained by this temporary baking, and $\{\{Ba(1-x)Cax\}O\}A(Ti(1-y)Zry)B O2$ It has the process which mixes the principal component containing the dielectric oxide of the presentation shown.

[0023] In the manufacture approach of the dielectric porcelain constituent concerning this invention, it has further the process which mixes the oxidation compound of Li, and the becoming compound preferably after the powder obtained at said temporary baking process, the oxidation compound of Li, and/or baking.

[0024] The electronic parts concerning this invention are electronic parts which have a dielectric layer. Said dielectric layer $\{\{Ba(1-x)Cax\}O\}A(Ti(1-y)Zry)B O2$ The principal component containing the dielectric oxide of the presentation shown, It has an accessory constituent including one or more kinds chosen from the compound which turns into these oxides after the oxide of Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P, and/or baking. said accessory constituent -- the constituent whole -- receiving -- oxide conversion -- 0.001-5-mol % -- it is contained and the notations A, Bx, and y which show the presentation ratio in the formula showing said principal component are characterized by having the relation of $0.990 \leq A/B < 1.000$, $0.01 \leq x \leq 0.25$, and $0.1 \leq y \leq 0.3$.

[0025] In the electronic parts concerning this invention, said dielectric layer contains the oxidation compound of Li, and 0.01-10000 ppm of becoming compounds by oxide (Li_2O) conversion after the oxidation compound of Li, and/or baking preferably.

[0026] The manufacture approach of the electronic parts concerning this invention Sr, Y, Gd, The process which carries out temporary baking of the accessory constituent including one or more kinds chosen from the compound which turns into these oxides after the oxide of Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P, and/or baking at 500-1000 degrees C beforehand, The fine particles obtained by this temporary baking, and $\{\{Ba(1-x)Cax\}O\}A(Ti(1-y)Zry)B O2$ The process which mixes the principal component containing the dielectric oxide of the presentation shown, It has the process which produces a dielectric paste using the mixed fine particles, the process which produces the paste for internal electrodes, the process which carries out the laminating of said dielectric paste and the paste for

internal electrodes by turns, and the process which calcinates said dielectric paste and the paste for internal electrodes by which the laminating was carried out by turns.

[0027] In the manufacture approach of the electronic parts concerning this invention, it has further the process which mixes the oxidation compound of Li, and the becoming compound preferably after the powder obtained at said temporary baking process, the oxidation compound of Li, and/or baking.

[0028]

[Function] Its accelerated aging of insulation resistance also improves more than 40 hour (200 degrees C, DC8v/micrometer) while being able to calcinate the dielectric porcelain constituent concerning this invention at 1000-1200-degree C low temperature. Moreover, in electronic parts, such as a chip capacitor which uses the dielectric porcelain constituent concerning this invention as a dielectric layer, the way piece and **** of an internal electrode decrease and the effectiveness which carries out reinforcement is acquired.

[0029] Moreover, by the manufacture approach of the dielectric porcelain constituent concerning this invention, though baking at low temperature is more possible than before, the high sintered compact of compactness is obtained.

[0030] Furthermore, by the manufacture approach of the electronic parts concerning this invention, though baking at low temperature is more possible than before, the dielectric layer which consists of the high sintered compact of compactness is obtained, moreover, the way piece and **** of an internal electrode decrease and the effectiveness which carries out reinforcement is acquired.

[0031]

[Embodiment of the Invention] Hereafter, this invention is explained based on the operation gestalt shown in a drawing. Drawing 1 is the important section sectional view of the stacked type ceramic condenser concerning 1 operation gestalt of this invention.

[0032] As shown in stacked type ceramic condenser Drawing 1, the stacked type ceramic condenser 1 as electronic parts concerning 1 operation gestalt of this invention has the capacitor element body 10 of a configuration of that the laminating of a dielectric layer 2 and the internal electrode layer 3 was carried out by turns. The external electrode 4 of the internal electrode layer 3 arranged by turns inside the component body 10 and the pair through which it flows respectively is formed in the both ends of this capacitor element body 10. Although there is especially no limit in the configuration of the capacitor element body 10, it usually considers as the shape of a rectangular parallelepiped. Moreover, although what is necessary is for there to be especially no limit also in the dimension, and just to consider as a suitable dimension according to an application, it is usually x(0.6-5.6mm) (0.3-5.0mm) x (0.3-1.9mm) extent.

[0033] The laminating of the internal electrode layer 3 has been carried out so that each end face may be exposed to the front face of two edges where the capacitor element body 10 counters by turns. It is formed in the both ends of the capacitor element body 10, it connects with the exposure end face of the internal electrode layer 3 arranged by turns, and the external electrode 4 of a pair constitutes a capacitor circuit.

[0034] Dielectric layer 2 dielectric layer 2 contains the dielectric porcelain constituent of this invention. The dielectric porcelain constituent of this invention is $\{ \{ Ba(1-x) Ca_x \} O \} A. (Ti(1-y) Zry) B O_2$ It has a principal component containing the dielectric oxide of the presentation expressed, and an accessory constituent including one or more kinds chosen from the oxide of Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P. Under the present circumstances, the amount of oxygen (O) may be deflected from the science stoichiometry presentation of the above-mentioned formula a little.

[0035] x are 0.10 or less [0.05 or more] preferably 0.25 or less [0.01 or more] among the above-mentioned formula. Moreover, y is 0.2 or less [0.1 or more] preferably 0.3 or less [0.1 or more]. Moreover, A/B is 0.999 or less [0.995 or more] preferably less than [0.990 or more] 1.000.

[0036] In this presentation, although x expresses calcium atomic number, this calcium acts as an element which raises an insulation resistance value while mainly acting as sintering stability. When x becomes less than 0.01, burning temperature becomes 1250 degrees C or more, and an insulation resistance value is 1×10^7 . If it will be less than omega and x exceeds 0.25, specific inductive capacity cannot be less than

8000, and it can be satisfied with neither of the cases of the basic property as a stacked type ceramic condenser. Therefore, the value of x has the desirable range of $0.01 \leq x \leq 0.25$.

[0037] In said empirical formula, although y expresses the atomic number of Zr, this Zr acts as a shifter which mainly moves the Curie point to a low temperature side. If dielectric loss will exceed 8% if y becomes less than 0.1, and y exceeds 0.3, specific inductive capacity cannot be less than 8000, and it can be satisfied with neither of the cases of the basic property as laminating ceramic KONDE \leq NSA. Therefore, the value of y has the desirable range of $0.1 \leq y \leq 0.3$.

[0038] If A/B becomes less than 0.99, while abnormality grain growth of a dielectric layer will arise in said empirical formula at the time of baking, an insulation resistance value is 1×10^7 . If it becomes under omega and A/B exceeds 1.00, a degree of sintering will fall and a precise sintered compact will not be obtained. Therefore, the range of A/B of $0.99 \leq A/B < 1.00$ is desirable. And a different point from the conventional dielectric porcelain constituent is in adding an accessory constituent in $A/B < 1$, and the point which adds Li oxidation compound.

[0039] Thus, by adding an accessory constituent, low-temperature baking can be attained without degrading the dielectric characteristics in the range of $A/B < 1$ of a principal component, the poor dependability at the time of carrying out lamination of the dielectric layer can be reduced, and reinforcement can be attained.

[0040] In this invention, if an accessory constituent becomes less than [0.001 mol %] to the whole constituent, a degree of sintering will fall and a precise sintered compact will not be obtained. Moreover, when five-mol % is exceeded, an insulation resistance value is 1×10^7 . It will be less than omega and the basic property as a stacked type ceramic condenser cannot be satisfied. this accessory constituent is chosen from the compound which turns into these oxides after the oxide of Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P, and/or baking -- one or more kinds are included three or more kinds preferably. this accessory constituent -- the constituent whole -- receiving -- oxide conversion -- it is -- 0.001-5-mol % -- it is contained. By including such an accessory constituent in the above-mentioned mol % range, the elevated-temperature load life of a ceramic condenser with the dielectric layer which calcinates a constituent and is obtained improves.

[0041] Preferably the compound which turns into an oxide by the oxide of manganese, and/or baking as an accessory constituent oxide (MnO) conversion -- 0.03-2-mol % -- desirable -- 0.2-1.3-mol % -- They are oxide (Y₂O₃) conversion about the compound which turns into an oxide more preferably by 0.2-0.4-mol the oxide of % and an yttrium and/or, and baking. They are oxide (V₂O₅) conversion preferably about 0.08-0.45-mol % and the compound which turns into an oxide more preferably by 0.2-0.4-mol the oxide of % and vanadium and/or, and baking. 0.05-0.5-mol % -- They are oxide (WO₃) conversion about 0.005-0.5-mol % and the compound which turns into an oxide preferably by 0.01-0.1-mol the oxide of % and a tungsten and/or, and baking. 0.005-0.3-mol % -- desirable -- 0.01-0.2-mol % -- more -- desirable -- about 0.01-0.1 mol % -- it contains. By making such an accessory constituent contain in the above-mentioned range, especially the degree of sintering in low temperature improves. Moreover, nickel oxide, Nb oxide, Mg oxide, Co oxide, Hf oxide, etc. may contain about 0.5 or less % of the weight as the sum total of an accessory constituent in addition to the above-mentioned accessory constituent.

[0042] Moreover, it is desirable to have added 0.01-15-mol % for the compound (for example, silicic acid compound of Li) which turns into an oxide of Li after the oxidation compound of Li and/or baking as sintering assistant ** by oxide (Li₂O) conversion to the whole constituent with the dielectric porcelain constituent concerning this invention.

[0043] These amounts are in the inclination for the electrical property of the ceramic condenser obtained to fall, while the degree of sintering of a dielectric porcelain constituent will fall, if it separates from the above-mentioned range. In addition, although you may add directly to a dielectric porcelain constituent, calcinating a dielectric porcelain constituent in the controlled atmosphere containing Li can also make Li oxide contain in the sintered compact obtained. However, it is desirable to include Li in a controlled atmosphere by 0.01-150000 ppm by oxide (Li₂O) conversion. When it comes to less than 0.01 ppm, a degree of sintering falls, and a precise sintered compact is not obtained. Moreover, when it exceeds

150000 ppm, an insulation resistance value is 1x107. It will be less than omega and the basic property as a stacked type ceramic condenser cannot be satisfied.

[0044] After carrying out temporary baking of the above-mentioned accessory constituent at 500-1000 degrees C beforehand, its approach of carrying out adding after mixing into a principal component is desirable to low-temperature baking, and its approach of carrying out adding after mixing of this accessory constituent and the oxidation compound of Li into a principal component is still more desirable to low-temperature baking.

[0045] As a result of measuring by atomic absorption analysis etc., the dielectric layers after baking obtained by these approaches are the oxide (Li₂O) conversion about Li, and it is still more preferably desirable preferably 1-5000, and to contain 1-500 ppm preferably especially 0.01-10000 ppm.

[0046] In addition, what is necessary is just to determine suitably terms and conditions shown in drawing 1, such as the number of laminatings of a dielectric layer 2, and thickness, according to the purpose or an application. Moreover, a dielectric layer 2 consists of a grain and 1% or less of a grain boundary phase, and a certain thing is [the mean particle diameter of the grain of a dielectric layer 2] desirable about 1-5 micrometers.

[0047] This grain boundary phase usually uses as a component the oxide of the quality of the material which constitutes dielectric materials or an internal electrode ingredient, the oxide of the quality of the material added separately, and the oxide of the quality of the material mixed as an impurity still in process, and usually consists of glass thru/or glassiness.

[0048] Although especially the electric conduction material contained in the internal electrode layer 3 internal-electrode layer 3 is not limited, since the component of a dielectric layer 2 has reducibility-proof, base metal can be used. As a base metal used as electric conduction material, nickel or nickel alloy is desirable. As a nickel alloy, the alloy of one or more sorts of elements and nickel which are chosen from Mn, Cr, Co, and aluminum is desirable, and, as for nickel content in an alloy, it is desirable that it is 95 % of the weight or more. In addition, in nickel or nickel alloy, various minor constituents, such as P, Fe, and Mg, may be contained about 0.1 or less % of the weight. Although what is necessary is just to determine the thickness of an internal electrode layer suitably according to an application etc., it is usually especially desirable that it is about 1-2.5 micrometers 0.5-5 micrometers.

[0049] Although especially the electric conduction material contained in the external electrode 4 external electrode 4 is not limited, Cu, Cu alloy, nickel, nickel alloy, etc. are usually used. In addition, of course, Ag, an Ag-Pd alloy, etc. are usable. In addition, cheap nickel, Cu(s), and these alloys are used with this operation gestalt. Although the thickness of an external electrode should just be suitably determined according to an application etc., it is usually desirable that it is about 10-50 micrometers.

[0050] The stacked type ceramic condenser using the dielectric porcelain constituent of manufacture approach this invention of a stacked type ceramic condenser is manufactured by printing or imprinting and calcinating an external electrode, after producing the Green chip by usual print processes and the usual sheet method using a paste and calcinating this like the conventional stacked type ceramic condenser. Hereafter, the manufacture approach is explained concretely.

[0051] The paste for dielectric layers may be the coating of the organic system which kneaded the dielectric raw material and the organic vehicle, and may be the coating of a drainage system.

[0052] According to the presentation of the dielectric porcelain constituent concerning this invention mentioned above, the raw material which constitutes a principal component, the raw material which constitutes an accessory constituent, and the raw material which constitutes sintering acid if needed are used for a dielectric raw material. As a raw material which constitutes a principal component, the compound which turns into an oxide by the oxide of Ti, Ba, Sr, calcium, and Zr and/or baking is used. it is chosen out of the compound which turns into an oxide by the oxide of Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P, and/or baking as a raw material which constitutes an accessory constituent -- three or more kinds of single oxides or multiple oxides are used preferably. [one or more kinds of] As a raw material which constitutes sintering acid, the compound which turns into an oxide by the oxide of Li and/or baking is used. As a compound which turns into an oxide by baking, a carbonate, a nitrate, an oxalate, an organometallic compound, etc. are illustrated, for example. Of course, an oxide and the

compound which turns into an oxide by baking may be used together.

[0053] As for these raw material powder, a thing with a mean particle diameter of about 0.0005-5 micrometers is usually used. What is necessary is just to perform it as follows, for example, for obtaining dielectric materials from such raw material powder.

[0054] First, a start raw material is blended with a predetermined quantitative ratio, for example, wet blending is carried out with a ball mill etc. Subsequently, it is made to dry with a spray dryer etc., temporary quenching is carried out after that, and the dielectric oxide of the above-mentioned formula which constitutes a principal component is obtained. In addition, 500-1000 degrees C of temporary quenching are 500-1300 degrees C usually preferably performed in air at 800-1000 degrees C still more preferably for about 2 to 10 hours. Subsequently, it grinds until a jet mill or a ball mill makes predetermined particle size, and dielectric materials are obtained. An accessory constituent and sintering acid (SiO₂ or Li₂O) carry out temporary baking of the principal component independently, and are mixed by the obtained dielectric materials, respectively. A desired property will not be acquired if it carries out also including an accessory constituent at the time of temporary baking of this principal component. Moreover, an accessory constituent and Li₂O temporary baking performed including O also reduces the effectiveness of low-temperature baking by half. An accessory constituent and Li₂O If temporary baking of the O is carried out at coincidence, Li compound will be generated and it will become remarkable highly reacting a fall or burning temperature with a principal component.

[0055] Additives, such as a binder used in case the paste for dielectric layers is adjusted, a plasticizer, a dispersant, and a solvent, may be various things. Moreover, a glass frit may be added for the paste for dielectric layers. As a binder, for example as a plasticizer, ethyl cellulose, abietic-acid resin, poly vinyl butyral, etc. for example, as a dispersant, an abietic-acid derivative, diethyl oxalic acid, a polyethylene glycol, a polyalkylene glycol, FUTARU acid ester, FUTARU acid dibutyl, etc. For example, a glycerol, an octadecyl amine, a trichloroacetic acid, oleic acid, As solvents, such as OKUTA diene, ethyl oleate, a mono-oleic acid glycerol, a triolein acid glycerol, glyceryl tristearate, and a MENSEDEN oil, toluene, a terpineol, butyl carbitol, a methyl ethyl ketone, etc. are mentioned, for example. A dispersant is made, and in case this paste is calcinated, the rate that dielectric materials occupy to the whole paste is made into about 50 - 80 % of the weight, in addition in a binder, a solvent makes a plasticizer about 20 - 50 % of the weight 0.01 to 5% of the weight 0.01 to 5% of the weight two to 5% of the weight. And said dielectric materials, these solvents, etc. are mixed, for example, it kneads with 3 rolls etc., and considers as a paste (slurry).

[0056] In addition, what is necessary is just to knead the drainage system vehicle made to dissolve a water-soluble binder, a water-soluble dispersant, etc. in water, and a dielectric raw material, in using the paste for dielectric layers as the coating of a drainage system. Especially the water-soluble binder used for a drainage system vehicle is not limited, for example, should just use polyvinyl alcohol, a cellulose, water-soluble acrylic resin, etc.

[0057] The paste for internal electrode layers kneads and prepares the various oxide used as the conductor ingredient which consists of various conductive metals or an alloy, or the conductor ingredient described above after baking, an organometallic compound, resinate, etc. and an organic vehicle.

[0058] Such mixture is used for nickel or nickel alloy pan as a conductor material used in case the paste for internal electrodes is manufactured. Especially a limit does not have such a conductor material in the configurations, such as the shape of a globular shape and a piece of Lynn, and the thing of these configurations may mix it. Moreover, 0.1-10 micrometers of about 0.1-1-micrometer things should just usually be preferably used for the mean particle diameter of conductor material.

[0059] An organic vehicle contains a binder and a solvent. As a binder, each well-known thing, such as ethyl cellulose, acrylic resin, and butyral resin, is usable, for example. A binder content is made into about 1 - 5 % of the weight. As a solvent, each well-known thing, such as a terpineol, butyl carbitol, and kerosine, is usable, for example. A solvent content is made into about 20 - 55 % of the weight to the whole paste.

[0060] Thus, the laminating of the paste for internal electrode layers and the paste for dielectric layers

which were obtained is carried out by turns by print processes, the replica method, the green sheet method, etc., respectively. When you use print processes, it exfoliates from a substrate and let them be a layered product, after carrying out laminating printing on substrates, such as PET, and cutting the paste for dielectric layers, and the paste for internal electrode layers in a predetermined configuration.

Moreover, when using the sheet method, after forming a green sheet using the paste for dielectric layers and printing the paste for internal electrode layers on this, the laminating of these is carried out and it considers as a layered product.

[0061] Next, after cutting the layered product obtained by doing in this way in predetermined layered product size, debinder processing and baking are performed. And in order to make a dielectric layer 2 reoxidate, it heat-treats.

[0062] Although what is necessary is just to perform debinder processing on condition that usual, when using base metal, such as nickel and nickel alloy, for the conductor ingredient of an internal electrode layer, it is desirable to carry out on condition that the following especially.

programming-rate: -- 5-300 degrees C/hour -- especially -- 10-50 degrees C/[an hour and] and retention temperature:200-400 degree C -- especially -- 250-350 degrees C, and holding-time:0.5 - 20 hours -- especially -- 1 - 10 hours, and ambient atmosphere : Inside of air.

[0063] The following conditions of baking conditions are desirable.

programming-rate: -- 50-500 degrees C/hour -- especially -- 200-300 degrees C/[an hour and] and retention temperature:1000-1200 degree C -- especially -- 1100-1200 degrees C, and holding-time:0.5 - 8 hours -- especially -- 1 - 3 hours, and cooling rate: -- N2 controlled atmosphere:humidification of was done especially an hour 200-300 degrees C /an hour 50-500 degrees C / H2 Mixed gas etc.

[0064] However, especially the oxygen tension in the air ambient atmosphere at the time of baking is 10-7 to 10-13 10 to 7 or less atms. It is desirable to carry out in atm. It is in the inclination for an internal electrode layer to oxidize if said range is exceeded, and when oxygen tension is too low not much, the electrode material of an internal electrode layer is in a lifting and the inclination which breaks off about abnormality sintering.

[0065] As for heat treatment after baking, it is desirable to perform retention temperature or a maximum temperature as 900-1100 degrees C. It is in the inclination for nickel of an internal electrode to oxidize if it is in the inclination for a life to become [the retention temperature at the time of heat treatment, or a maximum temperature] short since said under range of oxidation of dielectric materials is inadequate and said range is surpassed, and to react not only with capacity falling but with a dielectric base, and for a life to also become short. The oxygen tension in the case of heat treatment is 10-4-10-7atm more preferably 10 to 8 or more atms. It is desirable. Under in said range, when reoxidation of a dielectric layer 2 is difficult and surpasses said range, it is in the inclination for the internal electrode layer 3 to oxidize. And the following conditions of other heat treatment conditions are desirable.

[0066] holding-time: -- 0 - 6 hours -- especially -- 2 - 5 hours, and cooling rate: -- N2 gas:humidification of was especially done for ambient atmospheres an hour 100-300 degrees C /an hour 50-500 degrees C / Gas etc.

[0067] In addition, N2 What is necessary is just to use WETTA etc., in order to humidify gas, mixed gas, etc. In this case, about 0-75 degrees C of water temperature are desirable. Moreover, debinder processing, baking, and heat treatment may perform each continuously, or may be performed independently. It is desirable to change an ambient atmosphere after debinder processing, when it calcinates by having changed [without cooling] the ambient atmosphere and carried out the temperature up to the retention temperature in the case of baking continuously, it subsequently cools and the retention temperature of heat treatment is reached when performing these continuously, and to heat-treat. On the other hand, when performing these independently, baking is faced, and it is N2 to the retention temperature at the time of debinder processing. Gas or N2 humidified After it is desirable to change an ambient atmosphere and to continue a temperature up further, after carrying out a temperature up under a gas ambient atmosphere and it cools to the retention temperature at the time of annealing, it is N2 again. Gas or N2 humidified It is desirable to change into a gas ambient atmosphere and to continue cooling. Moreover, annealing is faced and it is N2. N2 which could change the ambient atmosphere and

humidified all the processes of annealing after carrying out a temperature up to retention temperature under a gas ambient atmosphere. It is good also as a gas ambient atmosphere.

[0068] Thus, end-face polish is given to the obtained sintered compact in barrel finishing, sand PURASUTO, etc., the paste for external electrodes can be burned on it, and the external electrode 4 is formed. The baking conditions of the paste for external electrodes are humidified N2, H2. It is desirable to consider as for [10 minutes] - about 1 hour at 600-800 degrees C in mixed gas. And a pad layer is formed by performing plating etc. on the external electrode 4 if needed. In addition, what is necessary is just to prepare the paste for external electrodes like the above-mentioned paste for internal electrode layers.

[0069] Thus, the stacked type ceramic condenser of manufactured this invention is mounted on a printed circuit board etc. with a pewter etc., and is used for various electronic equipment etc.

[0070] in addition, this invention is not limited to the operation gestalt mentioned above, within the limits of this invention, can be boiled variously and can be changed. For example, although the stacked type ceramic condenser was illustrated as electronic parts concerning this invention with the operation gestalt mentioned above, if it has the dielectric layer which it is not limited to a stacked type ceramic condenser, but is constituted from a dielectric porcelain constituent of the above-mentioned presentation as electronic parts concerning this invention, it is good anything.

[0071]

[Example] Hereafter, although this invention is explained based on a still more detailed example, this invention is not limited to these examples.

[0072] $\{\{Ba(1-x) Ca_x\} O\}$ A generated by sol gel composition as an example 1 start raw material $(Ti(1-y) Zr_y) B O_2$ The principal component which consists of the dielectric oxide of the presentation shown was used. The notations A, Bx, and y which show the presentation ratio in the formula showing a principal component suited the relation of the relation of $0.990 \leq A/B < 1.000$, $0.01 \leq x \leq 0.25$, and $0.1 \leq y \leq 0.3$. In addition, the mean particle diameter of the above-mentioned dielectric oxide was 0.4 micrometers, and the maximum grain size was 1.5 micrometers.

[0073] Moreover, $MnCO_3$ which is an accessory constituent $Y_2 O_3$ $V_2 O_5$ And WO_3 and SiO_2 As an additive (the mean particle diameter of 0.5 micrometers of the whole additive, maximum grain size 3.3) In the mole ratio shown in Table 1, on 900 degrees C and the conditions of 3 hours, wet grinding was respectively carried out with the ball mill for 16 hours, and temporary baking was carried out in the atmospheric-air ambient atmosphere, and after that, wet grinding was carried out with the ball mill for 20 hours for the crack, and it considered as the additive of an accessory constituent. And a principal component, an accessory constituent, and $Li_2 CO_3$ With the ball mill, wet grinding was carried out and the dielectric materials of the barium titanate system of sample numbers 1-34 shown in Table 1 were obtained for 16 hours. Moreover, it is Li_2 to an accessory constituent. CO_3 Except in addition having carried out temporary baking, it is the same approach as the above, and the dielectric materials of the barium titanate system of a sample number 35 shown in Table 1 were obtained.

[0074]

[Table 1]

試料No.	主成分 A/B	主成分 (モル)		含有量 (モル)					後添加 (mol%)
		X	Y	MnO	Y ₂ O ₃	VO ₂	WO ₃	SiO ₂	
1	1.000	0.08	0.20	0.372	0.111	0.06	0.037	0.59	0
2	1.014	0.07	0.20	0.377	0.24	0.69	0.039	0.587	0
3	1.014	0.07	0.20	0.377	0.24	0.69	0.039	0.587	0.05
4	1.014	0.07	0.20	0.377	0.24	0.69	0.039	0.587	0.3
5	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	1
6	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	5
7	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	15
8	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	25
9	0.997	0.08	0.20	0.35	0.289	0.059	0.034	0	0
10*	0.997	0.08	0.20	0.348	0.252	0.055	0.034	0	0.05
11*	0.997	0.08	0.20	0.348	0.252	0.055	0.034	0	0.3
12*	0.997	0.08	0.20	0.348	0.252	0.055	0.034	0	1
13*	0.997	0.09	0.20	0.348	0.252	0.055	0.034	0	5
14*	0.997	0.09	0.20	0.348	0.252	0.055	0.034	0	15
15	0.997	0.08	0.20	0.348	0.252	0.055	0.034	0	25
16*	0.991	0.08	0.21	0.352	0.259	0.04	0.034	0	3
17*	0.997	0.08	0.21	0.351	0.258	0.05	0.035	1.122	0.3
18*	0.996	0.08	0.20	0.352	0.285	0.044	0.037	0.753	1
19*	0.997	0.08	0.18	0.348	0.259	0.04	0.034	1.504	1
20	0.990	0.078	0.204	0.353	0.283	0.047	0.038	0.8	1
21	0.985	0.077	0.202	0.351	0.284	0.047	0.037	0.8	1
22	0.987	0.077	0.203	0.352	0.276	0.044	0.037	0.3	1
23	0.989	0.078	0.203	0.348	0.286	0.04	0.037	0.422	0.05
24	0.989	0.078	0.203	0.349	0.286	0.04	0.037	0.422	0.3
25	0.989	0.078	0.203	0.349	0.286	0.04	0.037	0.422	1
26	0.989	0.078	0.203	0.348	0.286	0.04	0.037	0.422	5
27	0.989	0.078	0.203	0.348	0.286	0.04	0.037	0.422	15
28	0.989	0.078	0.203	0.348	0.286	0.04	0.037	0.422	25
29	0.997	0.09	0.20	0.6	0.14	0.01	0.01	0.8	0.3
30	0.997	0.09	0.20	0.3	0.2	0.055	0.034	0.8	0.3
31	0.997	0.09	0.20	0.4	0.3	0.055	0.034	0.36	0.3
32	0.997	0.09	0.20	0.5	0.3	0.055	0.034	0.5	0.3
33	0.997	0.09	0.20	0.4	0.2	0.01	0.01	0.3	0.3
34	0.997	0.09	0.20	0.4	0.2	0.01	0.034	0	0.3
35	0.990	0.05	0.20	0.2	0.3	0.06	0.03	0.6	0.2

[0075] Using each of the dielectric materials of these sample numbers 1-35, with the compounding ratio shown below, ball mill mixing was carried out using the ball made from a zirconia, and it slurred and considered as the paste for dielectric layers. That is, it is the compounding ratio of the dielectric-materials:100 weight section, the acrylic resin:5.0 weight section, the benzyl-butyl-phthalate:2.5 weight section, the mineral spirit:6.5 weight section, the acetone:4.0 weight section, the trichloroethane:20.5 weight section, and the methylene chloride:41.5 weight section.

[0076] Next, with the compounding ratio shown below, it kneaded with 3 rolls, and it slurred and considered as the paste for internal electrodes. That is, they are the nickel:44.6 weight section, the terpineol:52 weight section, the ethyl cellulose:3 weight section, and the benzotriazol:0.4 weight section. Using these pastes, as it was the following, the laminating mold ceramic chip capacitor 1 shown in drawing 1 was manufactured.

[0077] First, the sheet of 16-micrometer thickness was formed with the doctor blade method etc. on the carrier film using the paste for dielectric layers, the paste for internal electrodes was used on this, and the internal electrode was printed. Then, the above-mentioned sheet was exfoliated from the carrier film, two or more sheet laminating of the sheet on which the internal electrode was inscribed was carried out,

and pressurization adhesion was carried out. In addition, the number of laminatings of a dielectric layer 2 was ten layers. Subsequently, after cutting a layered product in predetermined size, debinder processing, baking, and heat treatment were continuously performed on condition that the following. [0078] debinder processing programming-rate: -- 20 degrees C/[an hour and], retention temperature:250 degree C, holding-time:2 hours, and the object for ambient atmospheres -- gas:air. [0079] baking programming-rate: -- the temperature shown in retention temperature: of 200 degrees C /and each, and Table 2 an hour, holding-time:2 hours, and cooling temperature: -- N2 gas:humidification of was done for ambient atmospheres an hour 300 degrees C / H2 Mixed gas and oxygen tension:10-8atm.

[0080] heat treatment retention temperature: -- 1000 degrees C, holding-time:3 hours, and cooling temperature: -- N2 gas:humidification of was done for ambient atmospheres an hour 300 degrees C / Gas and oxygen tension:10-7atm.

[0081] In addition, it carried out to humidification of each gas for ambient atmospheres at the water temperature of 0-75 degrees C using WETTA.

[0082] After grinding the end face of the obtained sintered compact with sandblasting, the In-Ga alloy was applied and the electrode for a trial was formed. Thus, the size of the manufactured stacked capacitor 1 was 3.2mmx1.6mmx0.6mm, and the thickness of 10 micrometers and an internal electrode 3 of the thickness of a dielectric layer 2 was 2 micrometers.

[0083] The property of this stacked capacitor was inputted with the base temperature of 25 degrees C, the signal of the frequency of 1kHz and measurement electrical-potential-difference 1.0Vrms was inputted with the digital LCR meter (4274made from YHP A), and electrostatic capacity and dielectric loss tandelta were measured. Specific-inductive-capacity epsilonr of dielectric porcelain was computed in consideration of the sample dimension and electrostatic capacity of dielectric porcelain of a stacked capacitor.

[0084] In addition, to the stacked capacitor, the direct current voltage of 10V was impressed for 1 minute, and the insulation resistance value measured it. Moreover, the pressure up of the breakdown voltage was carried out by 3 V/S, and it measured the electrical potential difference on which the current 100mA or more flowed. As evaluation, in order to create the small capacitor of a high dielectric constant, specific-inductive-capacity epsilonr is an important property, and made 8000 or more good. Dielectric loss tandelta is an important property, in order to realize thin film-ization of a dielectric layer 2 and to create the small capacitor of a high dielectric constant, and it made 8% or less good. An insulation resistance value is 1x107. More than omega was made good. Breakdown voltage made good more than 100V (7v/(micrometer)). Moreover, these characteristic values were calculated from the average of the value measured using the n= 10 sample number of capacitors.

[0085] Moreover, the elevated-temperature load life (accelerated aging of insulation resistance) of a capacitor was measured by holding in the impression condition with a direct current voltage of 8v [/micrometer] at 200 degrees C. This elevated-temperature load life was performed about ten stacked capacitor samples, and was evaluated by measuring time amount until it results short from impression initiation of the capacitor which short-circuited first. It becomes especially important [life], in case an elevated-temperature load life carries out lamination of the dielectric layer, and time amount until it results short from impression initiation used 40 hours or more as the excellent article.

[0086] Moreover, it is the content of Li in the dielectric layer in each capacitor sample Li2 By O conversion, it measured by atomic absorption analysis. Furthermore, the capacitor sample was cut and it observed whether there would be any way piece of an internal electrode. These results were shown in Table 2.

[0087]

[Table 2]

試料No.	焼成温度 (°C)	比誘電率	誘電損失 (%)	絶縁抵抗 I/R (Ω)	破壊電圧 (V)	絶縁抵抗 高溫負荷 寿命 (h)	焼成後の 残存量 (ppm) Li:O	電極の逸切れ (△○,△)×
1	1250	12000	5	1.00E+10	428.8	30	0	×
2	1250	緻密な焼結体得られず	-	-	-	-	0	-
3	1250	緻密な焼結体得られず	-	-	-	-	5	-
4	1250	7000	4	1.00E+09	-	-	13	×
5	1250	6500	5	1.00E+09	-	-	76	×
6	1250	5400	6	1.00E+09	-	-	143	×
7	1250	2000	4	1.00E+09	-	-	423	×
8	1250	1500	7	1.00E+09	-	-	800	×
9	1250	600	30	1.00E+08	-	-	0	×
10*	1200	12000	4	1.00E+10	563	200	13	○
11*	1200	12000	4	1.00E+10	547	160	144	○
12*	1180	14000	6	1.00E+10	493	140	312	○
13*	1140	12000	6	1.00E+09	547	120	1623	○
14*	1100	10000	8	1.00E+08	483.3	110	6700	○
15	1050	7000	8	1.00E+08	568	144	12170	○
16*	1140	11000	4	1.00E+10	125	250	1248	○
17*	1140	12000	5	1.00E+10	110	220	139	○
18*	1180	14000	5	1.00E+10	561	220	404	○
19*	1140	12500	5	1.00E+10	483.8	200	453	○
20	1100	8000	10	1.00E+09	644	400	484	○
21	1050	異常粒成長	-	-	-	-	472	-
22	1200	異常粒成長	-	-	-	-	444	-
23	1100	異常粒成長	-	-	-	-	14	-
24	1100	異常粒成長	-	-	-	-	28	-
25	1050	異常粒成長	-	-	-	-	157	-
26	1050	異常粒成長	-	-	-	-	807	-
27	1050	異常粒成長	-	-	-	-	2077	-
28	1000	異常粒成長	-	-	-	-	31541	-
29	1140	10000	5.5	1.00E+09	483.3	250	849	○
30	1140	12000	4	1.00E+10	465	160	187	○
31	1180	14000	6	1.00E+10	655	84	180	○
32	1160	12000	6	1.00E+10	485	104	174	○
33	1200	10000	8	1.00E+09	483.3	108	201	○
34	1190	8000	8	1.00E+08	566	108	187	○
35	1250	8000	4.3	2.80E+10	423	40	118	×

[0088] In Table 1 and 2, * mark was put especially on the sample number equivalent to the desirable example of this invention. As shown in Table 1 and 2, the laminating mold ceramic chip capacitor of this invention is Li2 as sintering acid. Even if calcinated at the low temperature of 1140 degrees C by having used O, 8000 or more were the specific-inductive-capacity epsilonr. Moreover, Li2 as sintering acid Since the sintered compact with what [precise] has not added O (sample numbers 2 and 3) is not obtained, it turns out that the laminating mold ceramic chip capacitor of the degree of sintering in low temperature of this invention is improving.

[0089] When were independently experimented about the temporary baking temperature of an accessory constituent, and calcinated at the elevated temperature 1200 degrees C or more, the crack of an accessory constituent became difficult and it became clear that it was unsuitable forward.

[0090] Moreover, like a sample number 35, when temporary baking of an accessory constituent and the Li was carried out beforehand at coincidence, it was checked that the effectiveness of low-temperature baking decreases sharply. a sample number 35 is compared with a sample number 20, and coincidence understands it for them, when temporary baking of an accessory constituent and the Li is carried out beforehand -- as -- a near presentation -- burning temperature -- 100 degrees C or more -- going up -- an

electrode -- also breaking off -- being observed was checked.

[0091]

[Effect of the Invention] As explained above, the dielectric porcelain constituent which according to this invention has a high dielectric constant although baking at the temperature of 1200 degrees C or less is possible at a non-oxidizing atmosphere, and its manufacture approach can be offered. Moreover, according to this invention, low-temperature baking is possible and electronic parts, such as a chip capacitor whose accelerated aging of insulation resistance moreover improved, can be offered.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to amelioration, the electronic parts using the dielectric porcelain constituent as a dielectric layer, and those manufacture approaches of the dielectric porcelain constituent used as a dielectric layer of for example, a laminating mold ceramic condenser etc.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] Conventionally, a laminating mold ceramic condenser carries out the laminating of the green sheet of two or more sheets which printed conductive paste on the green sheet which consists of a predetermined dielectric porcelain constituent, and printed this conductive paste, calcinates a green sheet and an internal electrode in one, and is formed. And what is indicated by the patent number No. 2787746 of a high capacity ingredient for example, by the ceramic capacitor is conventionally known as a nonreducible dielectric porcelain constituent which can use base metal as an internal electrode.

[0003] The dielectric porcelain constituent indicated by this official report is $\{(Ba(1-x) Cax Sry) O\}$ A. $(Ti(1-z) Zrz) B O2$ Let the dielectric oxide shown be a principal component. However, it is $1.000 \leq A/B \leq 1.020$, $0.01 \leq x \leq 0.25$, $0 \leq y \leq 0.05$, and $0.05 \leq z \leq 0.20$.

[0004] However, in this dielectric porcelain constituent, a high burning temperature of 1220 degrees C or more is required for baking of what can suppress the reduction reaction of the dielectric materials generated at the time of baking.

[0005] Moreover, what is indicated by JP,10-279353,A, JP,6-14496,B, and JP,4-367559,A is known in recent years as a dielectric porcelain constituent in which low-temperature baking is possible. In JP,6-14496,B, it is $\{(Ba(1-x) Cax) O\}$ m. $(Ti(1-y-z) Zry Rz) O2-z/2$ The principal component with which it is expressed, and $SiO2$ $Li2$ The dielectric porcelain constituent which comes to calcinate mixture with the addition component which consists of O and MO (MO is BaO etc.) is indicated. However, R in a principal component is rare earth elements, such as Y, and is $1.00 \leq m \leq 1.04$.

[0006] Temporary baking of the principal component is carried out at 1200 degrees C, temporary quenching of the addition component is carried out to this official report at 1000 degrees C, the temporary-quenching powder of a principal component and an addition component is mixed, a slurry is formed with this mixed powder, and it fabricates in a predetermined configuration, and has indicated that a sintered compact is obtained by calcinating at 1150 degrees C.

[0007] Moreover, in JP,4-367559,A, it is $m(Ba(1-x) Cax) (Ti(1-y) Zry) n. O3$ The porcelain constituent expressed with $+aM1+bM2+cM3$ is indicated. However, as for compounds, such as Mn, and M2, M1 is [the compound of Si and M3] the compounds of Y.

[0008] this official report -- $BaCO3$ $CaCO3$ $TiO2$ $ZrO2$ $SiO2$ $Y2 O3$ etc. -- powder is mixed, temporary quenching of this powder is carried out at 1050-1240 degrees C, a Plastic solid is produced using this temporary-quenching powder, and it is indicated by calcinating at 1300-1400 degrees C that a sintered compact is obtained. In these dielectric porcelain constituents, even if it calcinates by the reducing atmosphere, porcelain is not returned, but a long lasting chip capacitor can be obtained.

[0009] Moreover, in JP,10-279353,A, it is $\{(Ba(1-x) Cax) O\}$ A. $(Ti(1-y) Zry) B O3$ It considers as a principal component and the dielectric porcelain constituent which contains the oxide of Y, Li, B, or Si as an accessory constituent is indicated. However, it is $0.990 \leq A/B \leq 1.02$, $0.01 \leq x \leq 0.10$, and $0.15 \leq y \leq 0.25$. Furthermore, in JP,11-130531,A, it is $\{(Ba(1-x) Cax) O\}$ A. $(Ti(1-y) Zry) B O3$ It considers as a principal component and the dielectric porcelain constituent which contains the oxide of Y, Si, Ba, and calcium as an accessory constituent is indicated. However, it is $0.98 \leq A/B \leq 1.01$,

0.01<=x<=0.10, and 0.15<=y<=0.25.

[0010] However, in the dielectric porcelain constituent shown in these official reports, while there was a problem in respect of lamination, technical problems, like burning temperature is high occurred.

[0011] A laminating mold ceramic chip capacitor carries out the laminating of the paste for internal electrodes, and the paste for dielectric layers by the sheet method, print processes, etc., really carries out coincidence baking, and is usually manufactured. Generally, although Pd and Pd alloy are used, since Pd is expensive, comparatively cheap nickel and nickel alloy are being used for an internal electrode. By the way, when forming an internal electrode with nickel or nickel alloy, if it calcinates in atmospheric air, an electrode will oxidize.

[0012] For this reason, generally after the debinder is calcinating by oxygen tension lower than the balanced oxygen tension of nickel and NiO. In this case, in order to attain eburnation of dielectric materials, it is usually SiO₂ as sintering acid. It is added. Moreover, in order to prevent the fall of the insulation resistance by reduction of a dielectric layer etc., addition, calcium permutation, etc. of Mn are performed.

[0013] However, compared with the laminating mold chip capacitor which has the internal electrode made from Pd calcinated and manufactured in atmospheric air, the laminating mold chip capacitor which has an internal electrode made from nickel or nickel alloy had the overwhelmingly short life of insulation resistance, and had the problem of being unreliable.

[0014] However, this problem contains the dielectric oxide which was proposed by this invention person etc. and which has a certain specific presentation as a principal component. The dielectric materials which carried out the amount addition of specification of the one or more kinds chosen from the compound which turns into these oxides after the oxide of Y, Gd, Tb, Dy, Zr, V, Mo, Zn, Cd, Ti, Sn, and P, and/or baking, It was mostly solvable with the laminating mold ceramic chip capacitor which carried out the laminating of the internal electrode material of nickel or nickel alloy, and calcinated it (JP,3-133116,A). That is, as shown in this official report, when adding Y etc. as an accessory constituent, compared with the chip capacitor with the conventional additive-free dielectric materials, the life increased by about 2 to 10 times, and it became clear that the dependability which was excellent to some extent was acquired.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, the dielectric porcelain constituent which according to this invention has a high dielectric constant although baking at the temperature of 1200 degrees C or less is possible at a non-oxidizing atmosphere, and its manufacture approach can be offered. Moreover, according to this invention, low-temperature baking is possible and electronic parts, such as a chip capacitor whose accelerated aging of insulation resistance moreover improved, can be offered.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, in a laminating mold ceramic chip capacitor equipped with the dielectric layer of the above presentations, there is a problem that eburnation is not carried out at less than 1400 degrees C, and it is SiO₂ as sintering acid at the former there. It used and low temperature-ized baking of the above-mentioned porcelain constituent was enabled.

[0016] However, it is [as opposed to / like before / a principal component (A/B<1)] SiO₂ as sintering acid. When a ratio was made [many], semi-conductor-ization was produced and there was a problem that insulation resistance was also low and accelerated aging was also short.

[0017] The purpose of this invention is offering the dielectric porcelain constituent which has a high dielectric constant, and its manufacture approach by the non-oxidizing atmosphere, although baking at the temperature of 1200 degrees C or less is possible. Moreover, low-temperature baking is possible for the purpose of this invention, and it is offering electronic parts, such as a chip capacitor whose accelerated aging of insulation resistance moreover improved.

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MEANS

[Means for Solving the Problem] In the dielectric porcelain constituent with which the artificer of this invention etc. is used as a dielectric layer of electronic parts, such as a laminating mold ceramic chip capacitor Compared with the dielectric porcelain constituent of addition, such as Y, baking at low temperature is enabled further and dependability is raised more to one layer. Moreover, by this high-reliability-ization As a result of examining wholeheartedly the dielectric porcelain constituent which makes lamination 10 micrometers or less possible for a dielectric layer, in the dielectric porcelain constituent of a specific presentation, it came to complete a header and this invention for the ability of the purpose of this invention to be attained by pinpointing the range of a presentation ratio.

[0019] Namely, the dielectric porcelain constituent concerning this invention $\{\{Ba(1-x)Cax[]\}O\}A(Ti(1-y)Zry)B O2$ The principal component containing the dielectric oxide of the presentation shown, It has an accessory constituent including one or more kinds chosen from the compound which turns into these oxides after the oxide of Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P, and/or baking. said accessory constituent -- the constituent whole -- receiving -- oxide conversion -- 0.001-5-mol % -- it is contained and the notations A, Bx, and y which show the presentation ratio in the formula showing said principal component are characterized by having the relation of $0.990 \leq A/B < 1.000$, $0.01 \leq x \leq 0.25$, and $0.1 \leq y \leq 0.3$.

[0020] the compound which turns into an oxidation compound of Li after the oxidation compound of Li, and/or baking to the whole constituent preferably in the dielectric porcelain constituent concerning this invention -- oxide ($Li_2 O$) conversion -- 0.01-15-mol % -- it contains.

[0021] In the dielectric porcelain constituent concerning this invention, the dielectric porcelain constituent after baking contains the oxidation compound of Li, and 0.01-10000 ppm of becoming compounds by oxide ($Li_2 O$) conversion after the oxidation compound of Li, and/or baking preferably. The content of the oxidation compound of Li and the becoming compound is measured by atomic absorption analysis etc. after the oxidation compound of Li in the dielectric porcelain constituent after baking, and/or baking.

[0022] The manufacture approach of the dielectric porcelain constituent concerning this invention The process which carries out temporary baking of the accessory constituent including one or more kinds chosen from the compound which turns into these oxides after the oxide of Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P, and/or baking at 500-1000 degrees C beforehand, The fine particles obtained by this temporary baking, and $\{\{Ba(1-x)Cax[]\}O\}A(Ti(1-y)Zry)B O2$ It has the process which mixes the principal component containing the dielectric oxide of the presentation shown.

[0023] In the manufacture approach of the dielectric porcelain constituent concerning this invention, it has further the process which mixes the oxidation compound of Li, and the becoming compound preferably after the powder obtained at said temporary baking process, the oxidation compound of Li, and/or baking.

[0024] The electronic parts concerning this invention are electronic parts which have a dielectric layer. Said dielectric layer $\{\{Ba(1-x)Cax[]\}O\}A(Ti(1-y)Zry)B O2$ The principal component containing the dielectric oxide of the presentation shown, It has an accessory constituent including one or more

kinds chosen from the compound which turns into these oxides after the oxide of Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P, and/or baking, said accessory constituent -- the constituent whole -- receiving -- oxide conversion -- 0.001-5-mol % -- it is contained and the notations A, Bx, and y which show the presentation ratio in the formula showing said principal component are characterized by having the relation of $0.990 \leq A/B \leq 1.000$, $0.01 \leq x \leq 0.25$, and $0.1 \leq y \leq 0.3$.

[0025] In the electronic parts concerning this invention, said dielectric layer contains the oxidation compound of Li, and 0.01-10000 ppm of becoming compounds by oxide (Li₂O) conversion after the oxidation compound of Li, and/or baking preferably.

[0026] The manufacture approach of the electronic parts concerning this invention Sr, Y, Gd, The process which carries out temporary baking of the accessory constituent including one or more kinds chosen from the compound which turns into these oxides after the oxide of Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P, and/or baking at 500-1000 degrees C beforehand, The fine particles obtained by this temporary baking, and $\{ \{ Ba(1-x) Ca_x \} O \} A (Ti(1-y) Zry) B O_2$ The process which mixes the principal component containing the dielectric oxide of the presentation shown, It has the process which produces a dielectric paste using the mixed fine particles, the process which produces the paste for internal electrodes, the process which carries out the laminating of said dielectric paste and the paste for internal electrodes by turns, and the process which calcinates said dielectric paste and the paste for internal electrodes by which the laminating was carried out by turns.

[0027] In the manufacture approach of the electronic parts concerning this invention, it has further the process which mixes the oxidation compound of Li, and the becoming compound preferably after the powder obtained at said temporary baking process, the oxidation compound of Li, and/or baking.

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OPERATION

[Function] Its accelerated aging of insulation resistance also improves more than 40 hour (200 degrees C, DC8v/micrometer) while being able to calcinate the dielectric porcelain constituent concerning this invention at 1000-1200-degree C low temperature. Moreover, in electronic parts, such as a chip capacitor which uses the dielectric porcelain constituent concerning this invention as a dielectric layer, the way piece and **** of an internal electrode decrease and the effectiveness which carries out reinforcement is acquired.

[0029] Moreover, by the manufacture approach of the dielectric porcelain constituent concerning this invention, though baking at low temperature is more possible than before, the high sintered compact of compactness is obtained.

[0030] Furthermore, by the manufacture approach of the electronic parts concerning this invention, though baking at low temperature is more possible than before, the dielectric layer which consists of the high sintered compact of compactness is obtained, moreover, the way piece and **** of an internal electrode decrease and the effectiveness which carries out reinforcement is acquired.

[0031]

[Embodiment of the Invention] Hereafter, this invention is explained based on the operation gestalt shown in a drawing. Drawing 1 is the important section sectional view of the stacked type ceramic condenser concerning 1 operation gestalt of this invention.

[0032] As shown in stacked type ceramic condenser drawing 1, the stacked type ceramic condenser 1 as electronic parts concerning 1 operation gestalt of this invention has the capacitor element body 10 of a configuration of that the laminating of a dielectric layer 2 and the internal electrode layer 3 was carried out by turns. The external electrode 4 of the internal electrode layer 3 arranged by turns inside the component body 10 and the pair through which it flows respectively is formed in the both ends of this capacitor element body 10. Although there is especially no limit in the configuration of the capacitor element body 10, it usually considers as the shape of a rectangular parallelepiped. Moreover, although what is necessary is for there to be especially no limit also in the dimension, and just to consider as a suitable dimension according to an application, it is usually x(0.6-5.6mm) (0.3-5.0mm) x (0.3-1.9mm) extent.

[0033] The laminating of the internal electrode layer 3 has been carried out so that each end face may be exposed to the front face of two edges where the capacitor element body 10 counters by turns. It is formed in the both ends of the capacitor element body 10, it connects with the exposure end face of the internal electrode layer 3 arranged by turns, and the external electrode 4 of a pair constitutes a capacitor circuit.

[0034] Dielectric layer 2 dielectric layer 2 contains the dielectric porcelain constituent of this invention. The dielectric porcelain constituent of this invention is $\{(Ba(1-x) Ca_x []) O\} A. (Ti(1-y) Zry) B O_2$ It has a principal component containing the dielectric oxide of the presentation expressed, and an accessory constituent including one or more kinds chosen from the oxide of Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P. Under the present circumstances, the amount of oxygen (O) may be deflected from the science stoichiometry presentation of the above-mentioned formula a little.

[0035] x are 0.10 or less [0.05 or more] preferably 0.25 or less [0.01 or more] among the above-mentioned formula. Moreover, y is 0.2 or less [0.1 or more] preferably 0.3 or less [0.1 or more]. Moreover, A/B is 0.999 or less [0.995 or more] preferably less than [0.990 or more] 1.000.

[0036] In this presentation, although x expresses calcium atomic number, this calcium acts as an element which raises an insulation resistance value while mainly acting as sintering stability. When x becomes less than 0.01, burning temperature becomes 1250 degrees C or more, and an insulation resistance value is 1×10^7 . If it will be less than omega and x exceeds 0.25, specific inductive capacity cannot be less than 8000, and it can be satisfied with neither of the cases of the basic property as a stacked type ceramic condenser. Therefore, the value of x has the desirable range of $0.01 \leq x \leq 0.25$.

[0037] In said empirical formula, although y expresses the atomic number of Zr, this Zr acts as a shifter which mainly moves the Curie point to a low temperature side. If dielectric loss will exceed 8% if y becomes less than 0.1, and y exceeds 0.3, specific inductive capacity cannot be less than 8000, and it can be satisfied with neither of the cases of the basic property as laminating ceramic KONDE \leq NSA. Therefore, the value of y has the desirable range of $0.1 \leq y \leq 0.3$.

[0038] If A/B becomes less than 0.99, while abnormality grain growth of a dielectric layer will arise in said empirical formula at the time of baking, an insulation resistance value is 1×10^7 . If it becomes under omega and A/B exceeds 1.00, a degree of sintering will fall and a precise sintered compact will not be obtained. Therefore, the range of A/B of $0.99 \leq A/B < 1.00$ is desirable. And a different point from the conventional dielectric porcelain constituent is in adding an accessory constituent in $A/B < 1$, and the point which adds Li oxidation compound.

[0039] Thus, by adding an accessory constituent, low-temperature baking can be attained without degrading the dielectric characteristics in the range of $A/B < 1$ of a principal component, the poor dependability at the time of carrying out lamination of the dielectric layer can be reduced, and reinforcement can be attained.

[0040] In this invention, if an accessory constituent becomes less than [0.001 mol %] to the whole constituent, a degree of sintering will fall and a precise sintered compact will not be obtained. Moreover, when five-mol % is exceeded, an insulation resistance value is 1×10^7 . It will be less than omega and the basic property as a stacked type ceramic condenser cannot be satisfied. this accessory constituent is chosen from the compound which turns into these oxides after the oxide of Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P, and/or baking -- one or more kinds are included three or more kinds preferably. this accessory constituent -- the constituent whole -- receiving -- oxide conversion -- it is -- 0.001-5-mol % -- it is contained. By including such an accessory constituent in the above-mentioned mol % range, the elevated-temperature load life of a ceramic condenser with the dielectric layer which calcinates a constituent and is obtained improves.

[0041] Preferably the compound which turns into an oxide by the oxide of manganese, and/or baking as an accessory constituent oxide (MnO) conversion -- 0.03-2-mol % -- desirable -- 0.2-1.3-mol % -- They are oxide (Y₂O₃) conversion about the compound which turns into an oxide more preferably by 0.2-0.4-mol the oxide of % and an yttrium and/or, and baking. They are oxide (V₂O₅) conversion preferably about 0.08-0.45-mol % and the compound which turns into an oxide more preferably by 0.2-0.4-mol the oxide of % and vanadium and/or, and baking. 0.05-0.5-mol % -- They are oxide (WO₃) conversion about 0.005-0.5-mol % and the compound which turns into an oxide preferably by 0.01-0.1-mol the oxide of % and a tungsten and/or, and baking. 0.005-0.3-mol % -- desirable -- 0.01-0.2-mol % -- more -- desirable -- about 0.01-0.1 mol % -- it contains. By making such an accessory constituent contain in the above-mentioned range, especially the degree of sintering in low temperature improves. Moreover, nickel oxide, Nb oxide, Mg oxide, Co oxide, Hf oxide, etc. may contain about 0.5 or less % of the weight as the sum total of an accessory constituent in addition to the above-mentioned accessory constituent.

[0042] Moreover, it is desirable to have added 0.01-15-mol % for the compound (for example, silicic acid compound of Li) which turns into an oxide of Li after the oxidation compound of Li and/or baking as sintering assistant ** by oxide (Li₂O) conversion to the whole constituent with the dielectric porcelain constituent concerning this invention.

[0043] These amounts are in the inclination for the electrical property of the ceramic condenser obtained to fall, while the degree of sintering of a dielectric porcelain constituent will fall, if it separates from the above-mentioned range. In addition, although you may add directly to a dielectric porcelain constituent, calcinating a dielectric porcelain constituent in the controlled atmosphere containing Li can also make Li oxide contain in the sintered compact obtained. However, it is desirable to include Li in a controlled atmosphere by 0.01-150000 ppm by oxide (Li₂O) conversion. When it comes to less than 0.01 ppm, a degree of sintering falls, and a precise sintered compact is not obtained. Moreover, when it exceeds 150000 ppm, an insulation resistance value is 1x10⁷. It will be less than omega and the basic property as a stacked type ceramic condenser cannot be satisfied.

[0044] After carrying out temporary baking of the above-mentioned accessory constituent at 500-1000 degrees C beforehand, its approach of carrying out adding after mixing into a principal component is desirable to low-temperature baking, and its approach of carrying out adding after mixing of this accessory constituent and the oxidation compound of Li into a principal component is still more desirable to low-temperature baking.

[0045] As a result of measuring by atomic absorption analysis etc., the dielectric layers after baking obtained by these approaches are the oxide (Li₂O) conversion about Li, and it is still more preferably desirable preferably 1-5000, and to contain 1-500 ppm preferably especially 0.01-10000 ppm.

[0046] In addition, what is necessary is just to determine suitably terms and conditions shown in drawing 1, such as the number of laminatings of a dielectric layer 2, and thickness, according to the purpose or an application. Moreover, a dielectric layer 2 consists of a grain and 1% or less of a grain boundary phase, and a certain thing is [the mean particle diameter of the grain of a dielectric layer 2] desirable about 1-5 micrometers.

[0047] This grain boundary phase usually uses as a component the oxide of the quality of the material which constitutes dielectric materials or an internal electrode ingredient, the oxide of the quality of the material added separately, and the oxide of the quality of the material mixed as an impurity still in process, and usually consists of glass thru/or glassiness.

[0048] Although especially the electric conduction material contained in the internal electrode layer 3 internal-electrode layer 3 is not limited, since the component of a dielectric layer 2 has reducibility-proof, base metal can be used. As a base metal used as electric conduction material, nickel or nickel alloy is desirable. As a nickel alloy, the alloy of one or more sorts of elements and nickel which are chosen from Mn, Cr, Co, and aluminum is desirable, and, as for nickel content in an alloy, it is desirable that it is 95 % of the weight or more. In addition, in nickel or nickel alloy, various minor constituents, such as P, Fe, and Mg, may be contained about 0.1 or less % of the weight. Although what is necessary is just to determine the thickness of an internal electrode layer suitably according to an application etc., it is usually especially desirable that it is about 1-2.5 micrometers 0.5-5 micrometers.

[0049] Although especially the electric conduction material contained in the external electrode 4 external electrode 4 is not limited, Cu, Cu alloy, nickel, nickel alloy, etc. are usually used. In addition, of course, Ag, an Ag-Pd alloy, etc. are usable. In addition, cheap nickel, Cu(s), and these alloys are used with this operation gestalt. Although the thickness of an external electrode should just be suitably determined according to an application etc., it is usually desirable that it is about 10-50 micrometers.

[0050] The stacked type ceramic condenser using the dielectric porcelain constituent of manufacture approach this invention of a stacked type ceramic condenser is manufactured by printing or imprinting and calcinating an external electrode, after producing the Green chip by usual print processes and the usual sheet method using a paste and calcinating this like the conventional stacked type ceramic condenser. Hereafter, the manufacture approach is explained concretely.

[0051] The paste for dielectric layers may be the coating of the organic system which kneaded the dielectric raw material and the organic vehicle, and may be the coating of a drainage system.

[0052] According to the presentation of the dielectric porcelain constituent concerning this invention mentioned above, the raw material which constitutes a principal component, the raw material which constitutes an accessory constituent, and the raw material which constitutes sintering acid if needed are used for a dielectric raw material. As a raw material which constitutes a principal component, the

compound which turns into an oxide by the oxide of Ti, Ba, Sr, calcium, and Zr and/or baking is used. it is chosen out of the compound which turns into an oxide by the oxide of Sr, Y, Gd, Tb, Dy, V, Mo, Zn, Cd, Ti, Sn, W, Mn, Si, and P, and/or baking as a raw material which constitutes an accessory constituent -- three or more kinds of single oxides or multiple oxides are used preferably. [one or more kinds of] As a raw material which constitutes sintering acid, the compound which turns into an oxide by the oxide of Li and/or baking is used. As a compound which turns into an oxide by baking, a carbonate, a nitrate, an oxalate, an organometallic compound, etc. are illustrated, for example. Of course, an oxide and the compound which turns into an oxide by baking may be used together.

[0053] As for these raw material powder, a thing with a mean particle diameter of about 0.0005-5 micrometers is usually used. What is necessary is just to perform it as follows, for example, for obtaining dielectric materials from such raw material powder.

[0054] First, a start raw material is blended with a predetermined quantitative ratio, for example, wet blending is carried out with a ball mill etc. Subsequently, it is made to dry with a spray dryer etc., temporary quenching is carried out after that, and the dielectric oxide of the above-mentioned formula which constitutes a principal component is obtained. In addition, 500-1000 degrees C of temporary quenching are 500-1300 degrees C usually preferably performed in air at 800-1000 degrees C still more preferably for about 2 to 10 hours. Subsequently, it grinds until a jet mill or a ball mill makes predetermined particle size, and dielectric materials are obtained. An accessory constituent and sintering acid (SiO₂ or Li₂O) carry out temporary baking of the principal component independently, and are mixed by the obtained dielectric materials, respectively. A desired property will not be acquired if it carries out also including an accessory constituent at the time of temporary baking of this principal component. Moreover, an accessory constituent and Li₂O Temporary baking performed including O also reduces the effectiveness of low-temperature baking by half. An accessory constituent and Li₂O If temporary baking of the O is carried out at coincidence, Li compound will be generated and it will become remarkable highly reacting a fall or burning temperature with a principal component.

[0055] Additives, such as a binder used in case the paste for dielectric layers is adjusted, a plasticizer, a dispersant, and a solvent, may be various things. Moreover, a glass frit may be added for the paste for dielectric layers. As a binder, for example as a plasticizer, ethyl cellulose, abietic-acid resin, poly vinyl butyral, etc. for example, as a dispersant, an abietic-acid derivative, diethyl oxalic acid, a polyethylene glycol, a polyalkylene glycol, FUTARU acid ester, FUTARU acid dibutyl, etc. For example, a glycerol, an octadecyl amine, a trichloroacetic acid, oleic acid, As solvents, such as OKUTA diene, ethyl oleate, a mono-oleic acid glycerol, a triolein acid glycerol, glyceryl tristearate, and a MENSEDEN oil, toluene, a terpineol, butyl carbitol, a methyl ethyl ketone, etc. are mentioned, for example. A dispersant is made, and in case this paste is calcinated, the rate that dielectric materials occupy to the whole paste is made into about 50 - 80 % of the weight, in addition in a binder, a solvent makes a plasticizer about 20 - 50 % of the weight 0.01 to 5% of the weight 0.01 to 5% of the weight two to 5% of the weight. And said dielectric materials, these solvents, etc. are mixed, for example, it kneads with 3 rolls etc., and considers as a paste (slurry).

[0056] In addition, what is necessary is just to knead the drainage system vehicle made to dissolve a water-soluble binder, a water-soluble dispersant, etc. in water, and a dielectric raw material, in using the paste for dielectric layers as the coating of a drainage system. Especially the water-soluble binder used for a drainage system vehicle is not limited, for example, should just use polyvinyl alcohol, a cellulose, water-soluble acrylic resin, etc.

[0057] The paste for internal electrode layers kneads and prepares the various oxide used as the conductor ingredient which consists of various conductive metals or an alloy, or the conductor ingredient described above after baking, an organometallic compound, resinate, etc. and an organic vehicle.

[0058] Such mixture is used for nickel or nickel alloy pan as a conductor material used in case the paste for internal electrodes is manufactured. Especially a limit does not have such a conductor material in the configurations, such as the shape of a globular shape and a piece of Lynn, and the thing of these configurations may mix it. Moreover, 0.1-10 micrometers of about 0.1-1-micrometer things should just

usually be preferably used for the mean particle diameter of conductor material.

[0059] An organic vehicle contains a binder and a solvent. As a binder, each well-known thing, such as ethyl cellulose, acrylic resin, and butyral resin, is usable, for example. A binder content is made into about 1 - 5 % of the weight. As a solvent, each well-known thing, such as a terpineol, butyl carbitol, and kerosine, is usable, for example. A solvent content is made into about 20 - 55 % of the weight to the whole paste.

[0060] Thus, the laminating of the paste for internal electrode layers and the paste for dielectric layers which were obtained is carried out by turns by print processes, the replica method, the green sheet method, etc., respectively. When you use print processes, it exfoliates from a substrate and let them be a layered product, after carrying out laminating printing on substrates, such as PET, and cutting the paste for dielectric layers, and the paste for internal electrode layers in a predetermined configuration.

Moreover, when using the sheet method, after forming a green sheet using the paste for dielectric layers and printing the paste for internal electrode layers on this, the laminating of these is carried out and it considers as a layered product.

[0061] Next, after cutting the layered product obtained by doing in this way in predetermined layered product size, debinder processing and baking are performed. And in order to make a dielectric layer 2 reoxidate, it heat-treats.

[0062] Although what is necessary is just to perform debinder processing on condition that usual, when using base metal, such as nickel and nickel alloy, for the conductor ingredient of an internal electrode layer, it is desirable to carry out on condition that the following especially.

programming-rate: -- 5-300 degrees C/hour -- especially -- 10-50 degrees C/[an hour and] and retention temperature:200-400 degree C -- especially -- 250-350 degrees C, and holding-time:0.5 - 20 hours -- especially -- 1 - 10 hours, and ambient atmosphere : Inside of air.

[0063] The following conditions of baking conditions are desirable.

programming-rate: -- 50-500 degrees C/hour -- especially -- 200-300 degrees C/[an hour and] and retention temperature:1000-1200 degree C -- especially -- 1100-1200 degrees C, and holding-time:0.5 - 8 hours -- especially -- 1 - 3 hours, and cooling rate: -- N2 controlled atmosphere:humidification of was done especially an hour 200-300 degrees C /an hour 50-500 degrees C / H2 Mixed gas etc.

[0064] However, especially the oxygen tension in the air ambient atmosphere at the time of baking is 10-7 to 10-13 10 to 7 or less atms. It is desirable to carry out in atm. It is in the inclination for an internal electrode layer to oxidize if said range is exceeded, and when oxygen tension is too low not much, the electrode material of an internal electrode layer is in a lifting and the inclination which breaks off about abnormality sintering.

[0065] As for heat treatment after baking, it is desirable to perform retention temperature or a maximum temperature as 900-1100 degrees C. It is in the inclination for nickel of an internal electrode to oxidize if it is in the inclination for a life to become [the retention temperature at the time of heat treatment, or a maximum temperature] short since said under range of oxidation of dielectric materials is inadequate and said range is surpassed, and to react not only with capacity falling but with a dielectric base, and for a life to also become short. The oxygen tension in the case of heat treatment is 10-4-10-7atm more preferably 10 to 8 or more atms. It is desirable. Under in said range, when reoxidation of a dielectric layer 2 is difficult and surpasses said range, it is in the inclination for the internal electrode layer 3 to oxidize. And the following conditions of other heat treatment conditions are desirable.

[0066] holding-time: -- 0 - 6 hours -- especially -- 2 - 5 hours, and cooling rate: -- N2 gas:humidification of was especially done for ambient atmospheres an hour 100-300 degrees C /an hour 50-500 degrees C / Gas etc.

[0067] In addition, N2 What is necessary is just to use WETTA etc., in order to humidify gas, mixed gas, etc. In this case, about 0-75 degrees C of water temperature are desirable. Moreover, debinder processing, baking, and heat treatment may perform each continuously, or may be performed independently. It is desirable to change an ambient atmosphere after debinder processing, when it calcinates by having changed [without cooling] the ambient atmosphere and carried out the temperature up to the retention temperature in the case of baking continuously, it subsequently cools and

the retention temperature of heat treatment is reached when performing these continuously, and to heat-treat. On the other hand, when performing these independently, baking is faced, and it is N2 to the retention temperature at the time of debinder processing. Gas or N2 humidified After it is desirable to change an ambient atmosphere and to continue a temperature up further, after carrying out a temperature up under a gas ambient atmosphere and it cools to the retention temperature at the time of annealing, it is N2 again. Gas or N2 humidified It is desirable to change into a gas ambient atmosphere and to continue cooling. Moreover, annealing is faced and it is N2. N2 which could change the ambient atmosphere and humidified all the processes of annealing after carrying out a temperature up to retention temperature under a gas ambient atmosphere It is good also as a gas ambient atmosphere.

[0068] Thus, end-face polish is given to the obtained sintered compact in barrel finishing, sand PURASUTO, etc., the paste for external electrodes can be burned on it, and the external electrode 4 is formed. The baking conditions of the paste for external electrodes are humidified N2. H2 It is desirable to consider as for [10 minutes] - about 1 hour at 600-800 degrees C in mixed gas. And a pad layer is formed by performing plating etc. on the external electrode 4 if needed. In addition, what is necessary is just to prepare the paste for external electrodes like the above-mentioned paste for internal electrode layers.

[0069] Thus, the stacked type ceramic condenser of manufactured this invention is mounted on a printed circuit board etc. with a pewter etc., and is used for various electronic equipment etc.

[0070] in addition, this invention is not limited to the operation gestalt mentioned above, within the limits of this invention, can be boiled variously and can be changed. For example, although the stacked type ceramic condenser was illustrated as electronic parts concerning this invention with the operation gestalt mentioned above, if it has the dielectric layer which it is not limited to a stacked type ceramic condenser, but is constituted from a dielectric porcelain constituent of the above-mentioned presentation as electronic parts concerning this invention, it is good anything.

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EXAMPLE

[Example] Hereafter, although this invention is explained based on a still more detailed example, this invention is not limited to these examples.

[0072] $\{ \{ \text{Ba}(1-x) \text{Ca}x \} \text{O} \}$ A generated by sol gel composition as an example 1 start raw material $(\text{Ti}(1-y) \text{Zr}y) \text{B O}_2$ The principal component which consists of the dielectric oxide of the presentation shown was used. The notations A, Bx, and y which show the presentation ratio in the formula showing a principal component suited the relation of the relation of $0.990 \leq A/B < 1.000$, $0.01 \leq x \leq 0.25$, and $0.1 \leq y \leq 0.3$. In addition, the mean particle diameter of the above-mentioned dielectric oxide was 0.4 micrometers, and the maximum grain size was 1.5 micrometers.

[0073] Moreover, MnCO_3 which is an accessory constituent $\text{Y}_2 \text{O}_3 \text{V}_2 \text{O}_5$ And WO_3 and SiO_2 As an additive (the mean particle diameter of 0.5 micrometers of the whole additive, maximum grain size 3.3) In the mole ratio shown in Table 1, on 900 degrees C and the conditions of 3 hours, wet grinding was respectively carried out with the ball mill for 16 hours, and temporary baking was carried out in the atmospheric-air ambient atmosphere, and after that, wet grinding was carried out with the ball mill for 20 hours for the crack, and it considered as the additive of an accessory constituent. And a principal component, an accessory constituent, and $\text{Li}_2 \text{CO}_3$ With the ball mill, wet grinding was carried out and the dielectric materials of the barium titanate system of sample numbers 1-34 shown in Table 1 were obtained for 16 hours. Moreover, it is Li_2 to an accessory constituent. CO_3 Except in addition having carried out temporary baking, it is the same approach as the above, and the dielectric materials of the barium titanate system of a sample number 35 shown in Table 1 were obtained.

[0074]

[Table 1]

試料No.	主成分	主成分 (モル)		含有量 (モル)					後添加 (mol%)
		A/B	X	Y	MnO	VO _{2.0}	VO _{2.0}	WO ₃	SiO ₂
1	1.000	0.08	0.20	0.372	0.111	0.06	0.037	0.59	0
2	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	0
3	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	0.05
4	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	0.3
5	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	1
6	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	5
7	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	15
8	1.014	0.07	0.20	0.377	0.24	0.59	0.039	0.587	25
9	0.997	0.08	0.20	0.35	0.259	0.059	0.034	0	0
10*	0.997	0.08	0.20	0.348	0.252	0.056	0.034	0	0.05
11*	0.997	0.08	0.20	0.348	0.252	0.055	0.034	0	0.3
12*	0.997	0.08	0.20	0.348	0.252	0.055	0.034	0	1
13*	0.997	0.09	0.20	0.348	0.252	0.055	0.034	0	5
14*	0.997	0.09	0.20	0.348	0.252	0.055	0.034	0	15
15	0.997	0.08	0.20	0.348	0.252	0.055	0.034	0	25
16*	0.991	0.09	0.21	0.352	0.259	0.04	0.034	0	3
17*	0.997	0.08	0.21	0.351	0.258	0.05	0.035	1.122	0.3
18*	0.998	0.08	0.20	0.352	0.258	0.044	0.037	0.753	1
19*	0.997	0.09	0.18	0.348	0.259	0.04	0.034	1.804	1
20	0.980	0.078	0.204	0.353	0.283	0.047	0.038	0.8	1
21	0.985	0.077	0.202	0.351	0.284	0.047	0.037	0.8	1
22	0.987	0.077	0.203	0.352	0.276	0.044	0.037	0.3	1
23	0.989	0.078	0.203	0.349	0.286	0.04	0.037	0.422	0.05
24	0.989	0.078	0.203	0.349	0.286	0.04	0.037	0.422	0.3
25	0.989	0.078	0.203	0.349	0.286	0.04	0.037	0.422	1
26	0.989	0.078	0.203	0.349	0.286	0.04	0.037	0.422	5
27	0.989	0.078	0.203	0.348	0.286	0.04	0.037	0.422	15
28	0.989	0.078	0.203	0.349	0.286	0.04	0.037	0.422	25
29	0.997	0.09	0.20	0.6	0.14	0.01	0.01	0.8	0.3
30	0.997	0.09	0.20	0.3	0.2	0.055	0.034	0.8	0.3
31	0.997	0.09	0.20	0.4	0.3	0.055	0.034	0.36	0.3
32	0.997	0.09	0.20	0.5	0.3	0.055	0.034	0.5	0.3
33	0.997	0.09	0.20	0.4	0.2	0.01	0.01	0.3	0.3
34	0.997	0.09	0.20	0.4	0.2	0.01	0.034	0	0.3
35	0.990	0.05	0.20	0.2	0.2	0.06	0.03	0.8	0.2

[0075] Using each of the dielectric materials of these sample numbers 1-35, with the compounding ratio shown below, ball mill mixing was carried out using the ball made from a zirconia, and it slurred and considered as the paste for dielectric layers. That is, it is the compounding ratio of the dielectric-materials:100 weight section, the acrylic resin:5.0 weight section, the benzyl-butyl-phthalate:2.5 weight section, the mineral spirit:6.5 weight section, the acetone:4.0 weight section, the trichloroethane:20.5 weight section, and the methylene chloride:41.5 weight section.

[0076] Next, with the compounding ratio shown below, it kneaded with 3 rolls, and it slurred and considered as the paste for internal electrodes. That is, they are the nickel:44.6 weight section, the terpineol:52 weight section, the ethyl cellulose:3 weight section, and the benzotriazol:0.4 weight section. Using these pastes, as it was the following, the laminating mold ceramic chip capacitor 1 shown in drawing 1 was manufactured.

[0077] First, the sheet of 16-micrometer thickness was formed with the doctor blade method etc. on the carrier film using the paste for dielectric layers, the paste for internal electrodes was used on this, and the internal electrode was printed. Then, the above-mentioned sheet was exfoliated from the carrier film, two or more sheet laminating of the sheet on which the internal electrode was inscribed was carried out,

and pressurization adhesion was carried out. In addition, the number of laminatings of a dielectric layer 2 was ten layers. Subsequently, after cutting a layered product in predetermined size, debinder processing, baking, and heat treatment were continuously performed on condition that the following.

[0078] debinder processing programming-rate: -- 20 degrees C/[an hour and], retention temperature:250 degree C, holding-time:2 hours, and the object for ambient atmospheres -- gas:air.

[0079] baking programming-rate: -- the temperature shown in retention temperature: of 200 degrees C /and each, and Table 2 an hour, holding-time:2 hours, and cooling temperature: -- N2 gas:humidification of was done for ambient atmospheres an hour 300 degrees C / H2 Mixed gas and oxygen tension:10-8atm.

[0080] heat treatment retention temperature: -- 1000 degrees C, holding-time:3 hours, and cooling temperature: -- N2 gas:humidification of was done for ambient atmospheres an hour 300 degrees C / Gas and oxygen tension:10-7atm.

[0081] In addition, it carried out to humidification of each gas for ambient atmospheres at the water temperature of 0-75 degrees C using WETTA.

[0082] After grinding the end face of the obtained sintered compact with sandblasting, the In-Ga alloy was applied and the electrode for a trial was formed. Thus, the size of the manufactured stacked capacitor 1 was 3.2mmx1.6mmx0.6mm, and the thickness of 10 micrometers and an internal electrode 3 of the thickness of a dielectric layer 2 was 2 micrometers.

[0083] The property of this stacked capacitor was inputted with the base temperature of 25 degrees C, the signal of the frequency of 1kHz and measurement electrical-potential-difference 1.0Vrms was inputted with the digital LCR meter (4274made from YHP A), and electrostatic capacity and dielectric loss tandelta were measured. Specific-inductive-capacity epsilonr of dielectric porcelain was computed in consideration of the sample dimension and electrostatic capacity of dielectric porcelain of a stacked capacitor.

[0084] In addition, to the stacked capacitor, the direct current voltage of 10V was impressed for 1 minute, and the insulation resistance value measured it. Moreover, the pressure up of the breakdown voltage was carried out by 3 V/S, and it measured the electrical potential difference on which the current 100mA or more flowed. As evaluation, in order to create the small capacitor of a high dielectric constant, specific-inductive-capacity epsilonr is an important property, and made 8000 or more good. Dielectric loss tandelta is an important property, in order to realize thin film-ization of a dielectric layer 2 and to create the small capacitor of a high dielectric constant, and it made 8% or less good. An insulation resistance value is 1x10⁷. More than omega was made good. Breakdown voltage made good more than 100V (7v/(micrometer)). Moreover, these characteristic values were calculated from the average of the value measured using the n= 10 sample number of capacitors.

[0085] Moreover, the elevated-temperature load life (accelerated aging of insulation resistance) of a capacitor was measured by holding in the impression condition with a direct current voltage of 8v [/micrometer] at 200 degrees C. This elevated-temperature load life was performed about ten stacked capacitor samples, and was evaluated by measuring time amount until it results short from impression initiation of the capacitor which short-circuited first. It becomes especially important [life], in case an elevated-temperature load life carries out lamination of the dielectric layer, and time amount until it results short from impression initiation used 40 hours or more as the excellent article.

[0086] Moreover, it is the content of Li in the dielectric layer in each capacitor sample Li2 By O conversion, it measured by atomic absorption analysis. Furthermore, the capacitor sample was cut and it observed whether there would be any way piece of an internal electrode. These results were shown in Table 2.

[0087]

[Table 2]

試料No.	焼成温度 (°C)	比説電率	説電損失 (%)	絶縁抵抗 I R (Ω)	破壊電圧 (V)	絶縁抵抗 高溫負荷 寿命 (h)	焼成後の 残存量 (ppm) Li ₂ O	電極の迷切れ	
								(ガガ、ア)×	(ガガ、ア)×
1	1250	12000	6	1.00E+10	426.6	30	0	×	
2	1250	緻密な焼結体得られず	-	-	-	-	0	-	
3	1250	緻密な焼結体得られず	-	-	-	-	5	-	
4	1250	7000	4	1.00E+09	-	-	13	×	
5	1250	6500	5	1.00E+09	-	-	78	×	
6	1250	5400	6	1.00E+09	-	-	143	×	
7	1250	2000	4	1.00E+09	-	-	423	×	
8	1250	1500	7	1.00E+09	-	-	800	×	
9	1250	500	30	1.00E+08	-	-	0	×	
10*	1200	12000	4	1.00E+10	563	200	13	○	
11*	1200	12000	4	1.00E+10	547	160	144	○	
12*	1180	14000	6	1.00E+10	493	140	312	○	
13*	1140	12000	6	1.00E+09	547	120	1823	○	
14*	1100	10000	8	1.00E+09	483.3	110	5700	○	
15	1050	7000	8	1.00E+08	568	144	12170	○	
16*	1140	11000	4	1.00E+10	125	250	1246	○	
17*	1140	12000	6	1.00E+10	110	220	139	○	
18*	1180	14000	6	1.00E+10	551	220	404	○	
19*	1140	12500	5	1.00E+10	483.8	200	453	○	
20	1100	8000	10	1.00E+09	644	400	484	○	
21	1080	異常粒成長	-	-	-	-	472	-	
22	1200	異常粒成長	-	-	-	-	444	-	
23	1100	異常粒成長	-	-	-	-	14	-	
24	1100	異常粒成長	-	-	-	-	28	-	
25	1050	異常粒成長	-	-	-	-	157	-	
26	1050	異常粒成長	-	-	-	-	907	-	
27	1050	異常粒成長	-	-	-	-	2077	-	
28	1000	異常粒成長	-	-	-	-	31541	-	
29	1140	10000	5.5	1.00E+09	483.3	250	849	○	
30	1140	12000	4	1.00E+10	455	160	187	○	
31	1180	14000	6	1.00E+10	655	84	180	○	
32	1160	12000	6	1.00E+10	485	104	174	○	
33	1200	10000	8	1.00E+09	483.3	108	201	○	
34	1180	8000	8	1.00E+08	568	106	197	○	
35	1250	8000	4.3	2.80E+10	423	40	118	×	

[0088] In Table 1 and 2, * mark was put especially on the sample number equivalent to the desirable example of this invention. As shown in Table 1 and 2, the laminating mold ceramic chip capacitor of this invention is Li₂ as sintering acid. Even if calcinated at the low temperature of 1140 degrees C by having used O, 8000 or more were the specific-inductive-capacity epsilon. Moreover, Li₂ as sintering acid Since the sintered compact with what [precise] has not added O (sample numbers 2 and 3) is not obtained, it turns out that the laminating mold ceramic chip capacitor of the degree of sintering in low temperature of this invention is improving.

[0089] When were independently experimented about the temporary baking temperature of an accessory constituent, and calcinated at the elevated temperature 1200 degrees C or more, the crack of an accessory constituent became difficult and it became clear that it was unsuitable forward.

[0090] Moreover, like a sample number 35, when temporary baking of an accessory constituent and the Li was carried out beforehand at coincidence, it was checked that the effectiveness of low-temperature baking decreases sharply. a sample number 35 is compared with a sample number 20, and coincidence understands it for them, when temporary baking of an accessory constituent and the Li is carried out beforehand -- as -- a near presentation -- burning temperature -- 100 degrees C or more -- going up -- an

electrode -- also breaking off -- being observed was checked.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing 1 is the sectional view of the stacked type ceramic condenser concerning 1 operation gestalt of this invention.

[Description of Notations]

- 1 -- Stacked type ceramic condenser
- 10 -- Capacitor element body
- 2 -- Dielectric layer
- 3 -- Internal electrode layer
- 4 -- External electrode

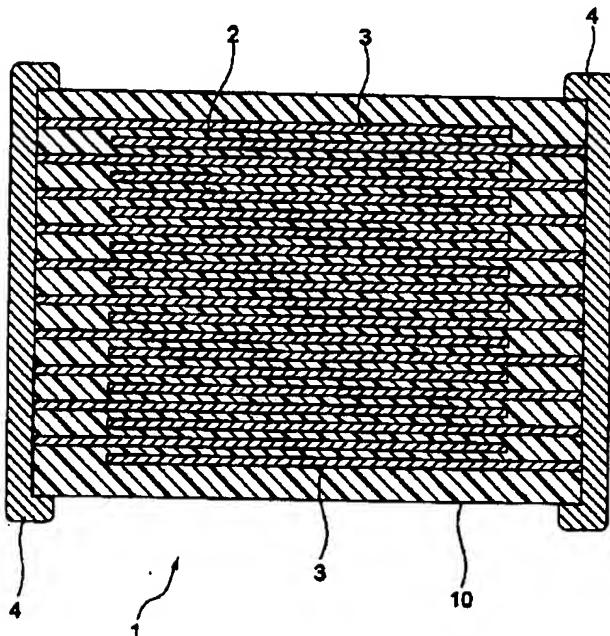
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DRAWINGS

[Drawing 1]

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